LA-UR-17-27949
Approved for public release; distribution is unlimited.

Title: Synthesis of Actinide Materials for the Study of Basic Actinide Science and Rapid Separation of Fission Products

Author(s): Dorhout, Jacquelyn Marie

Intended for: Thesis defense presentation

Issued: 2017-09-05

Synthesis of Actinide Materials for the Study of Basic Actinide Science and Rapid Separation of Fission Products

Jacquelyn M. Dorhout

Dissertation Defense

September 29, 2017

Outline

- Nuclear Forensics Story pt.1
  - Background
  - UO_2 target manufacturing
  - Irradiation and Results
- Nuclear Forensics Story pt. 2
  - MOF background
  - MOF target manufacturing
  - Irradiation and Results
- Conclusions
- Organoactinide Chemistry Story
  - Actinide Chalcogenides
  - C-X bond activation using actinides
- Summation of Projects
- Future Work
- Acknowledgements

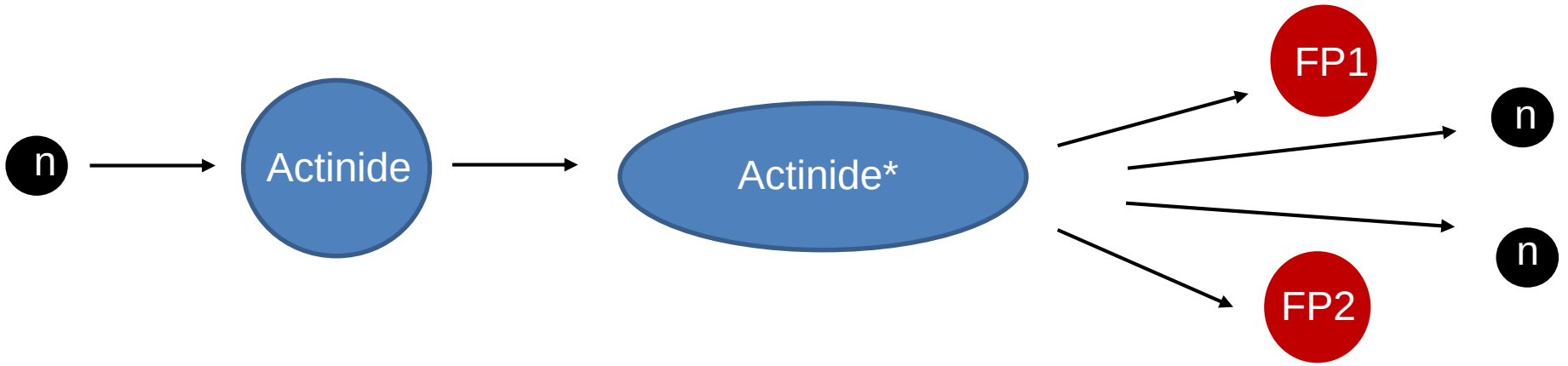
Nuclear Forensics Part 1

UO_2 Target Materials

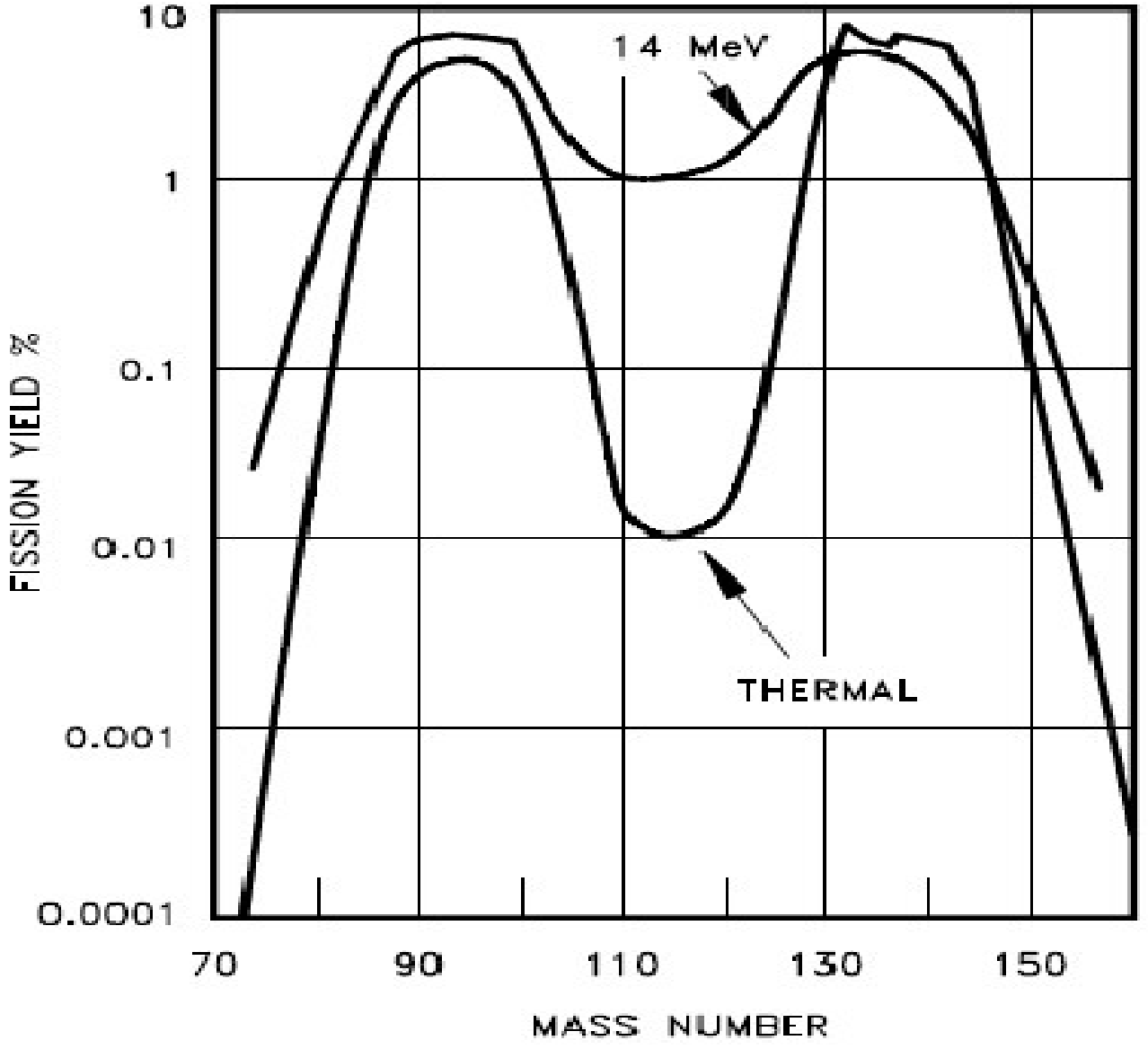
Background – Nuclear Forensics

- Nuclear forensics – evaluation of isotopic signatures to determine the identification of a device post-detonation
  - These signatures and their ratios are different depending on the type of device
  - Leads to information on when/how/where it was made
- These isotopic signatures are produced from the fission of the starting material

Background - Fission



Background - Fission



Prelas, M. A.; Weaver, C. L.; Watermann, M. L.; Lukosi, E. D.; Schott, R. J.; Wisniewski, D. A. *Progress in Nuclear Energy* **2014**, *75*, 117.

Background - Goal

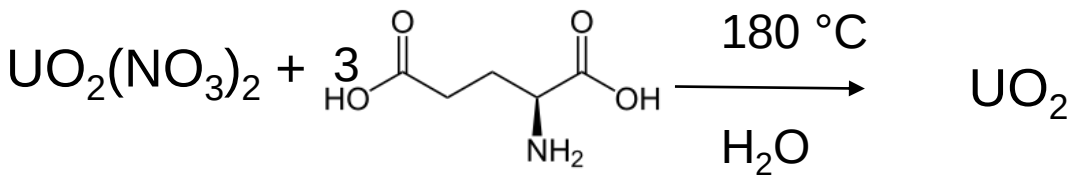
- Goal: To create actinide target materials for the rapid separation of fission products without the need to dissolve the entire target
  - Proof-of-principle to advance the library of fission product ratios for various actinides
- Procedure: To prepare and irradiate a target material, then rapidly separate and measure the fission products

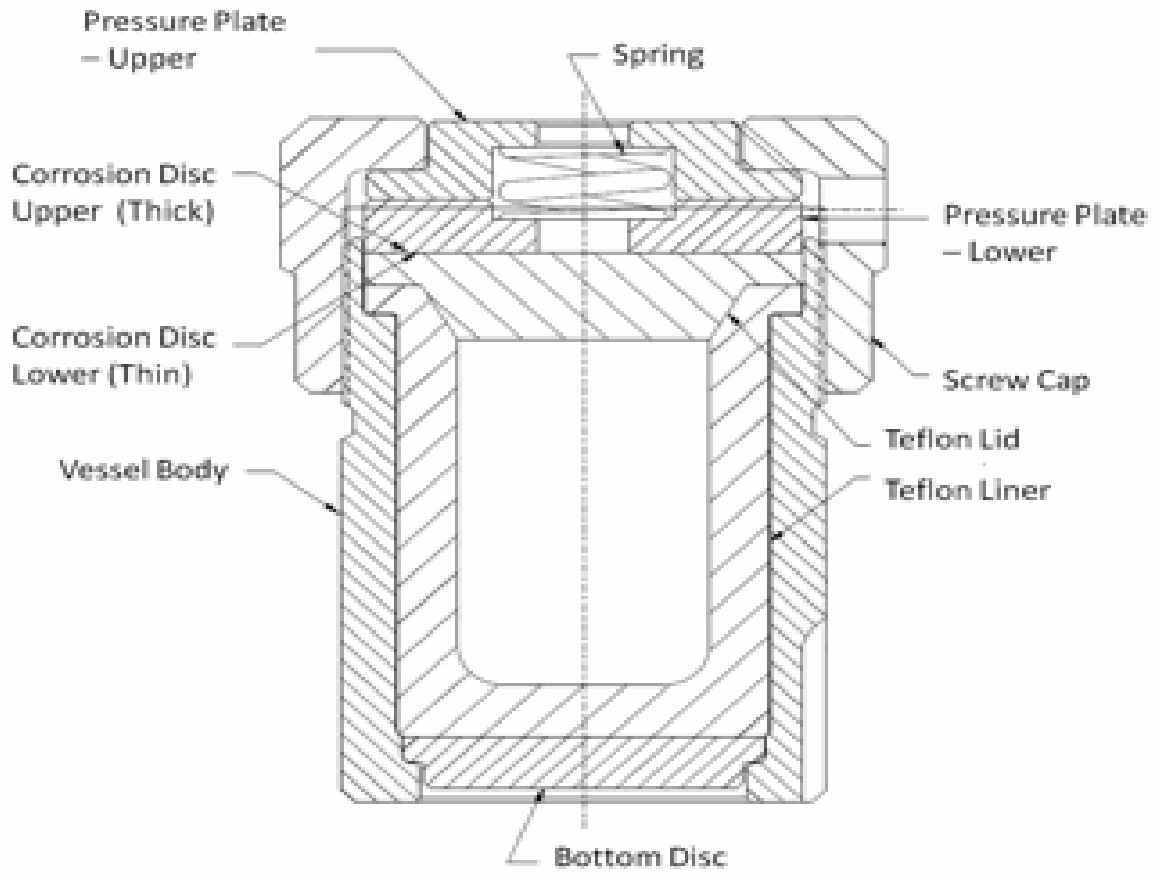
Background – UO_2

- UO_2 has been used in fuel, target materials, and fission product analysis for decades
  - Literature references site these particle sizes between 20 µm and 200 mm
- Dissolution of materials is generally done in HNO_3 and/or HCl at acid concentrations > 1M

Methods – UO_2 Production

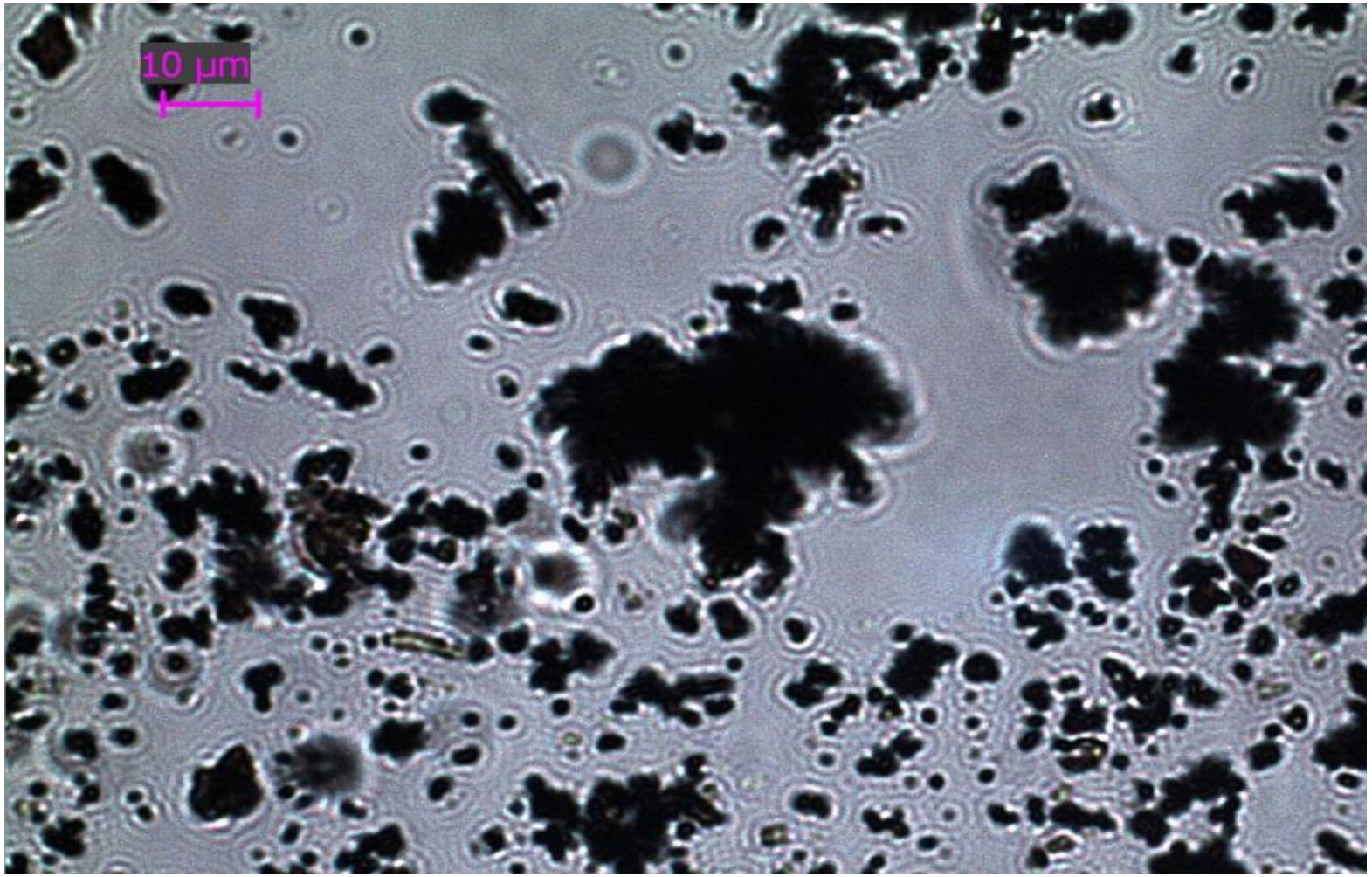
- Hydrothermal synthesis





Blakemore, P.; Oregon State University: Corvallis, Oregon, 2017; Vol. 2017, p image of parr bomb.

Methods – UO_2 Production

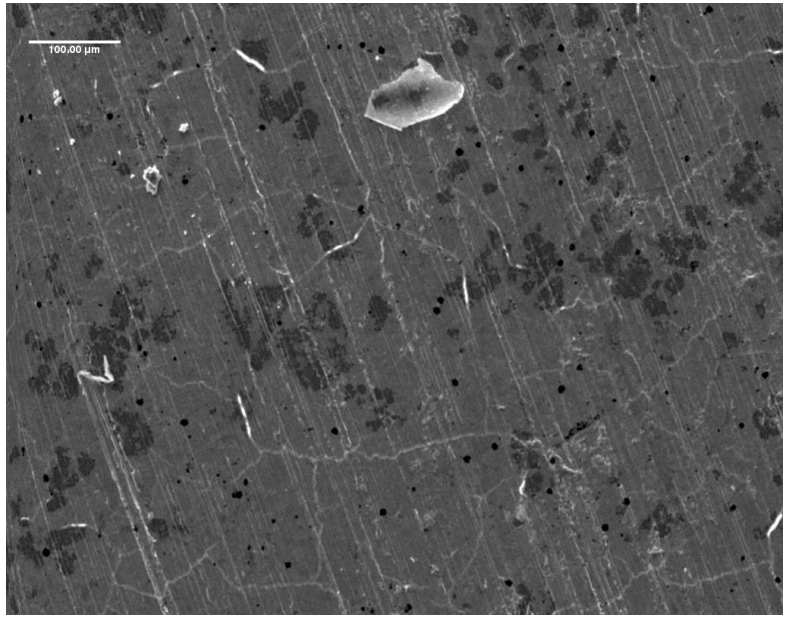


Methods – UO_2 Dissolution

- Remember – we don't want to dissolve the material
- Microparticles of UO_2 were contacted with acids to determine which would be used for future fission product extraction
  - 1M, 0.01 M HCl and 0.01 M HNO_3 tested
  - ICP-MS used to calculate concentration of uranium in acid after 24 hours
  - Unsurprisingly, lower concentrations of acids dissolved less uranium
- Acids chosen for experiments: 0.01 M, 0.1 M HCl; 0.01 M, 0.1 M HNO_3

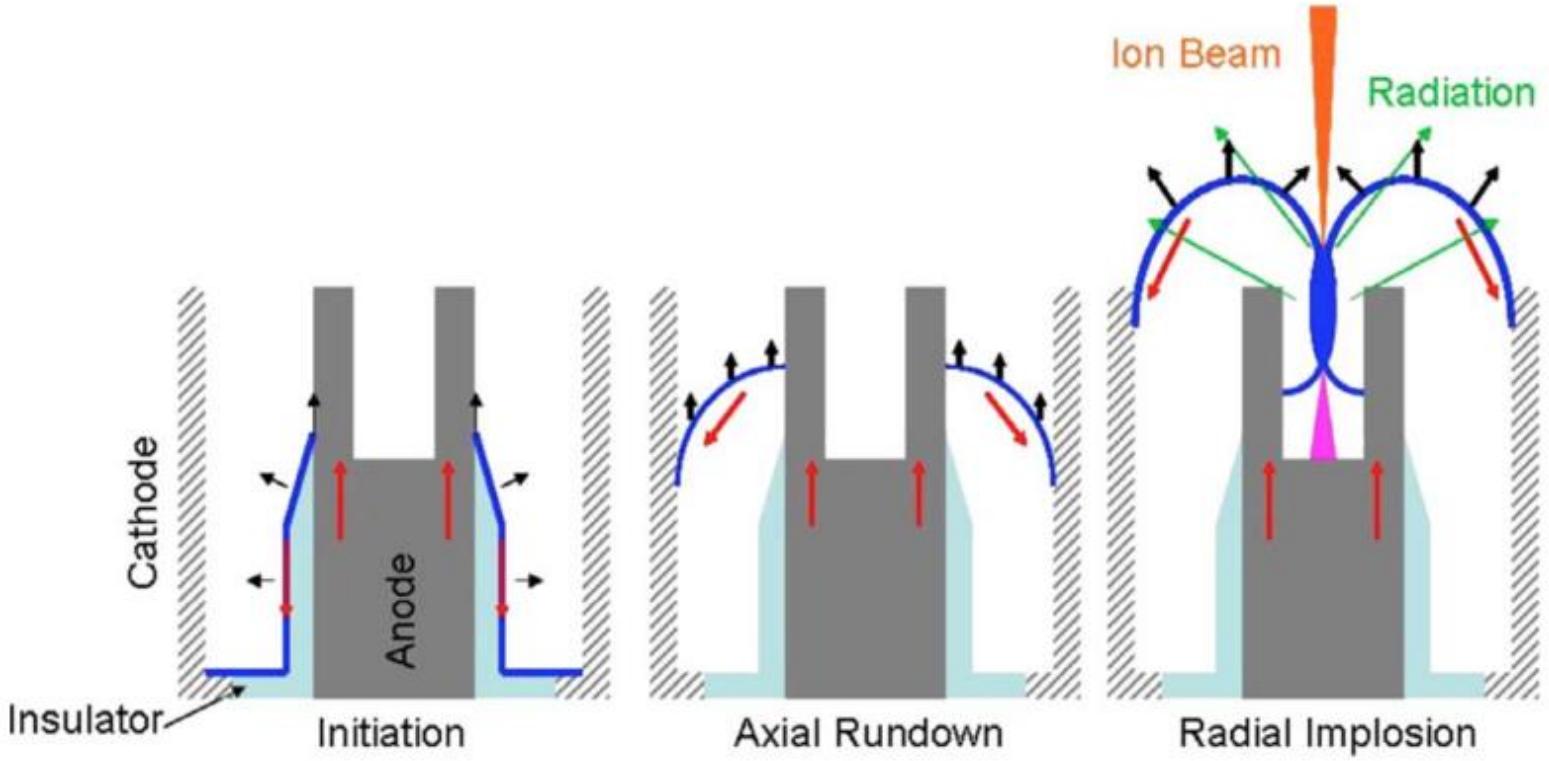
Methods – UO_2 Target Production

- KBr chosen as a secondary matrix to trap fission products
  - 3:1 ratio of KBr:UO_2 gave best homogeneity by optical spectroscopy and SEM analysis



Methods – DPF Irradiation

- Dense Plasma Focus (DPF) – neutron source from D-D plasma

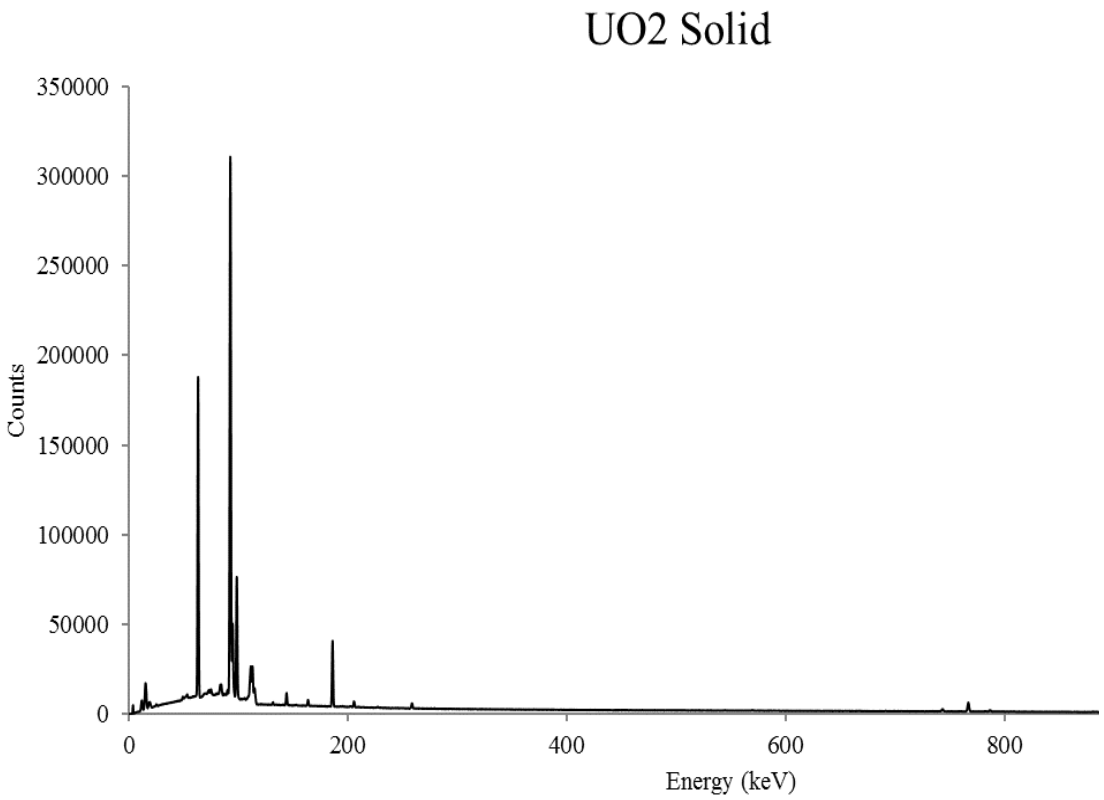


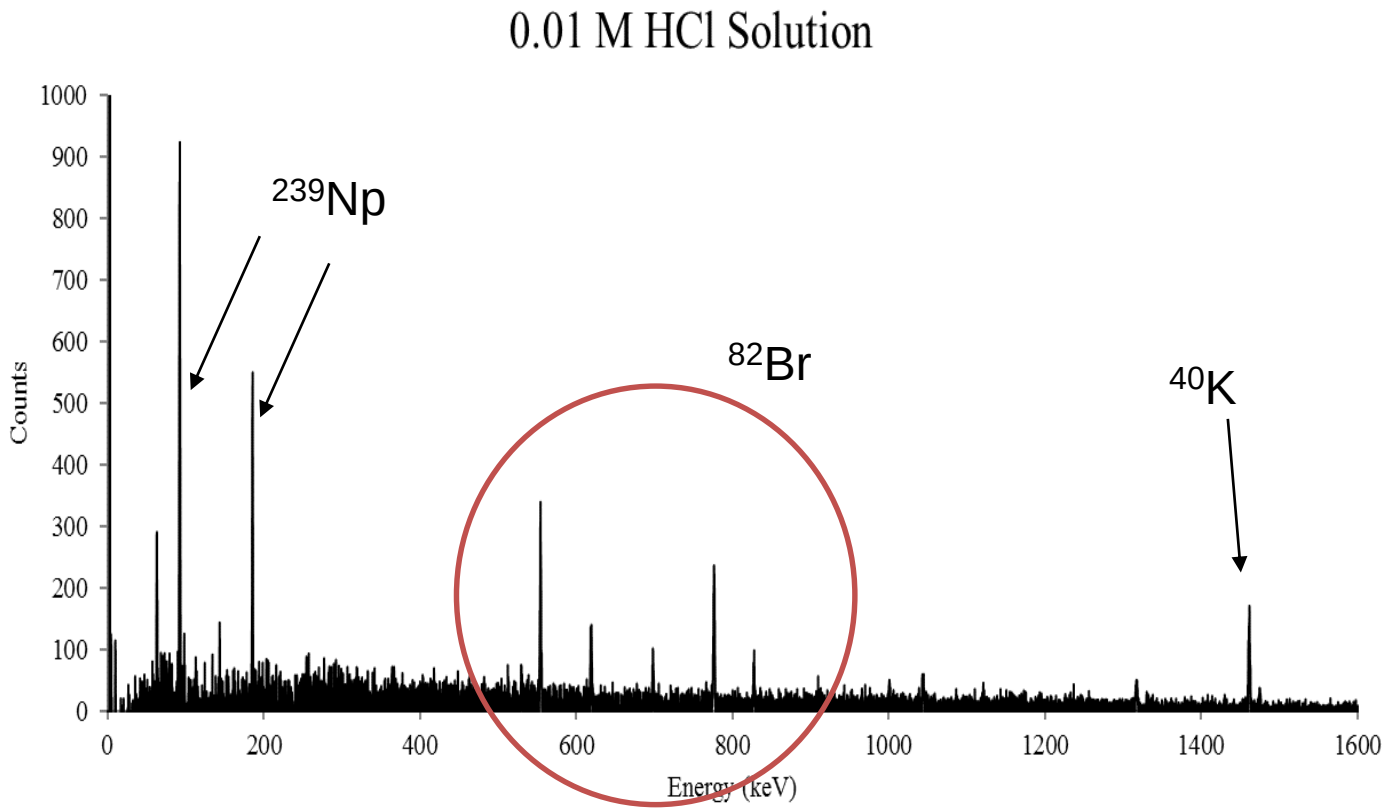
Krishnan, M. *IEEE Transactions on Plasma Science* **2012**, *40*, 3189.

Methods – UO_2 Target Production for DPF

- Roughly 230 mg of dUO_2 mixed with 890 mg of KBr pressed into pellets and flame sealed in glass
  - 5:1 ratio was chosen to increase the amount of material within the target
- Irradiated at DPF

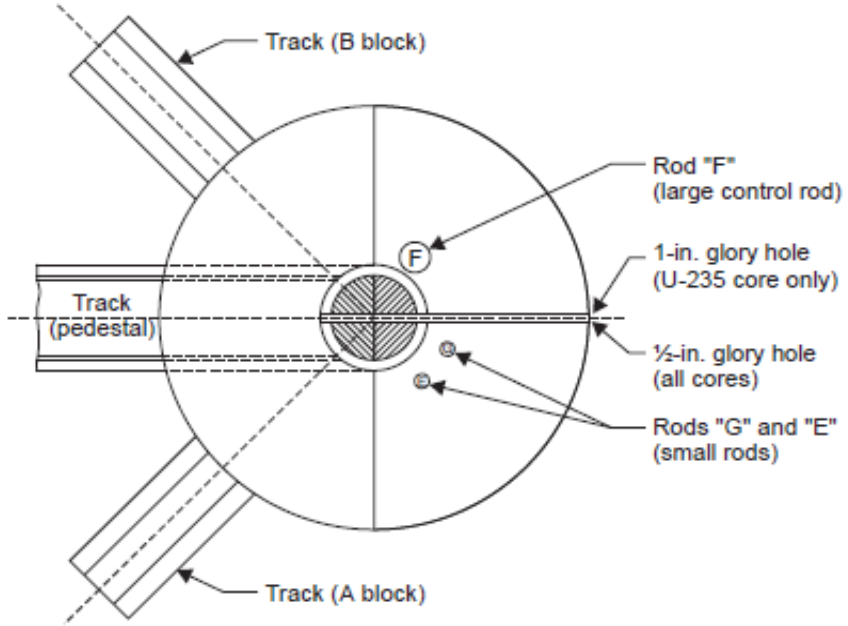
Results - DPF

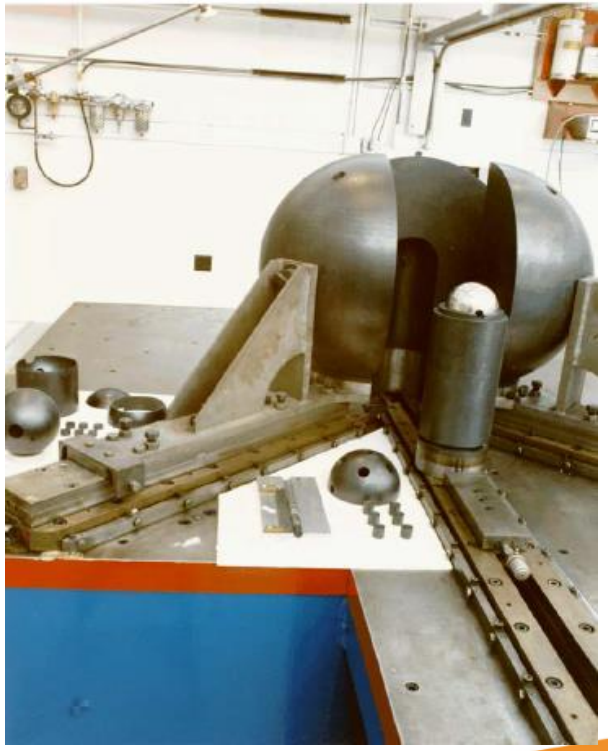

UO2 Solid
Counts
Energy (keV)
350000
300000
250000
200000
150000
100000
50000
0
0
200
400
600
800


0.01 M HCl Solution
Counts
Energy (keV)
239Np
82Br
40K
1000
900
800
700
600
500
400
300
200
100
0
0
200
400
600
800
1000
1200
1400
1600

Methods - Irradiation

- Flattop is a critical assembly device made of HEU
- Sample holders are loaded into “Glory Hole”

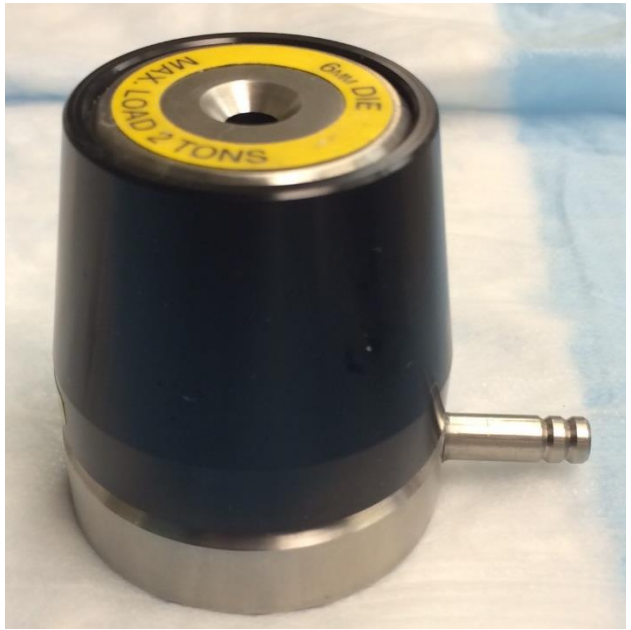




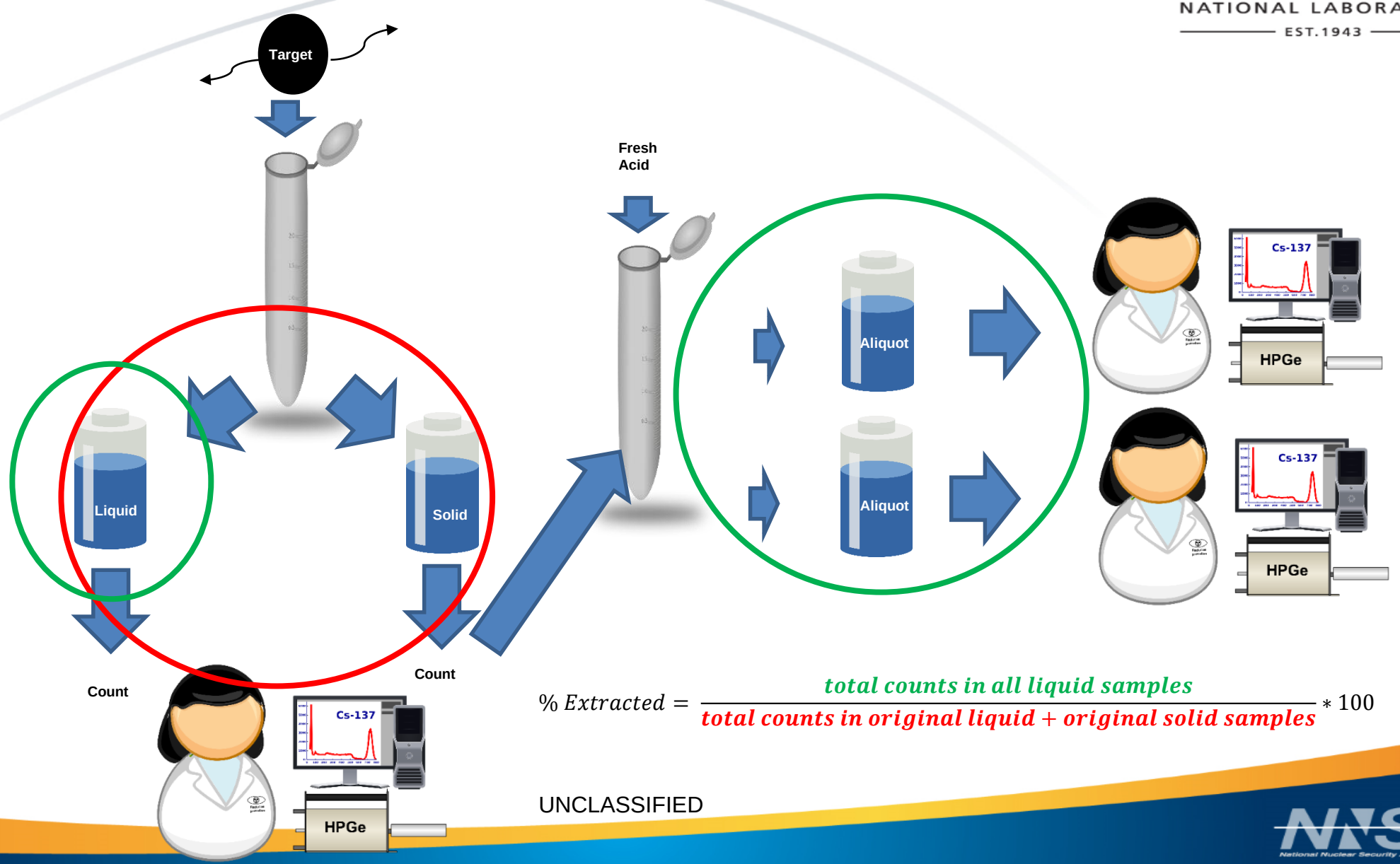
Brewer, R. W.; McLaughlin, T. P.; Dean, V. *Uranium-235 Sphere Reflected by Normal Uranium Using Flattop*, Nuclear Energy Agency, 1999.

Methods – UO_2 Target Production for Flattop

- All targets had roughly 25 mg dUO_2 unless otherwise noted
- 3KBr:UO_2 mixture pressed into a 6 mm pellet using a KBr die
- Pellet wrapped in Al foil to prevent dispersion
- Sealed in Al sample holder



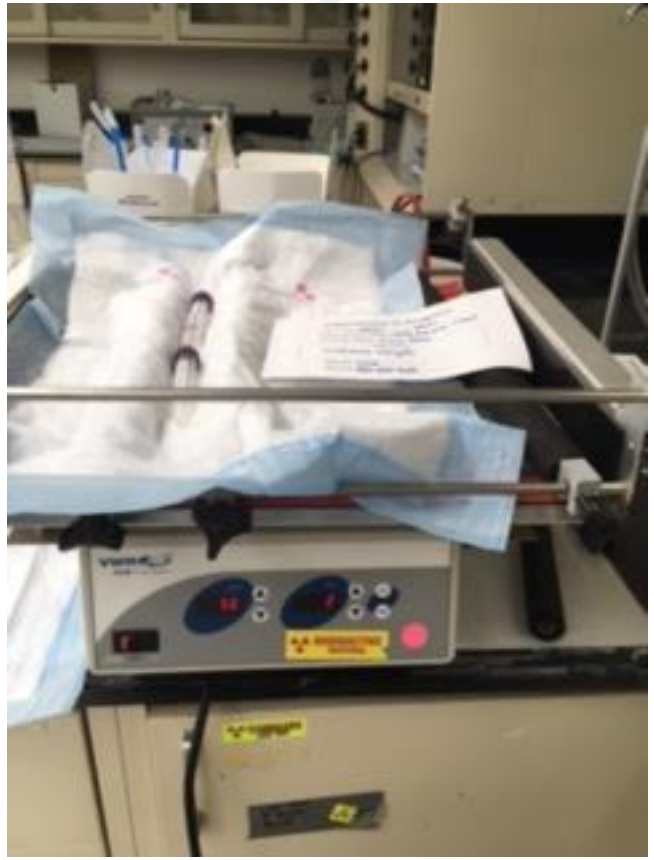
Method – Rapid Separation

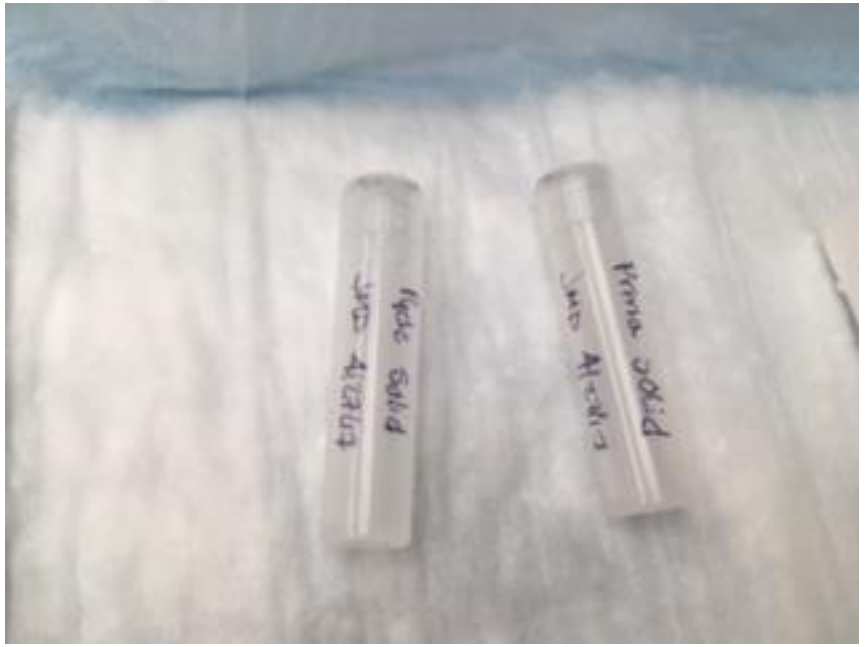


$$\% \, Extracted = \frac{total\ counts\ in\ all\ liquid\ samples}{total\ counts\ in\ original\ liquid + original\ solid\ samples} * 100$$

UNCLASSIFIED

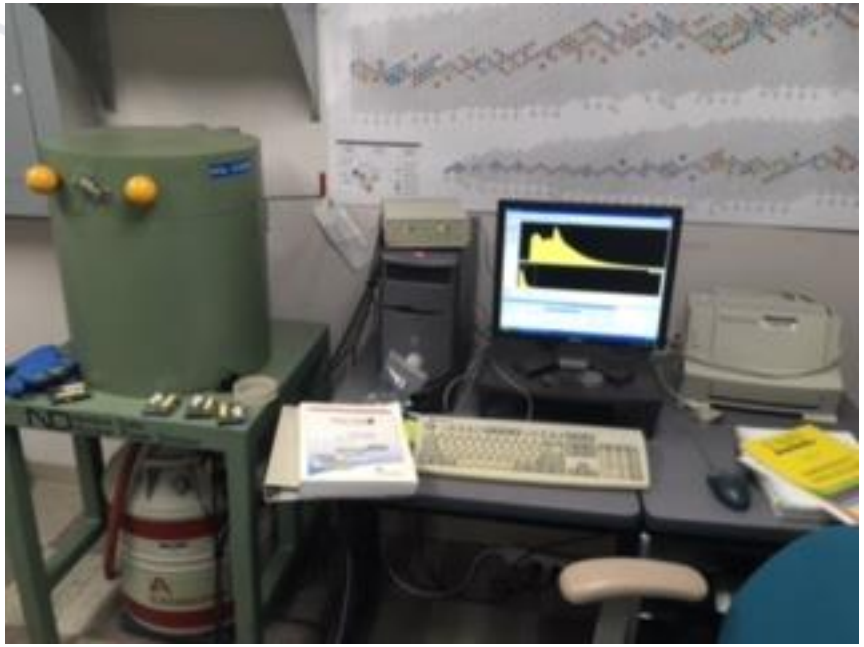
Methods – Rapid Separation





Methods – Gamma Counting

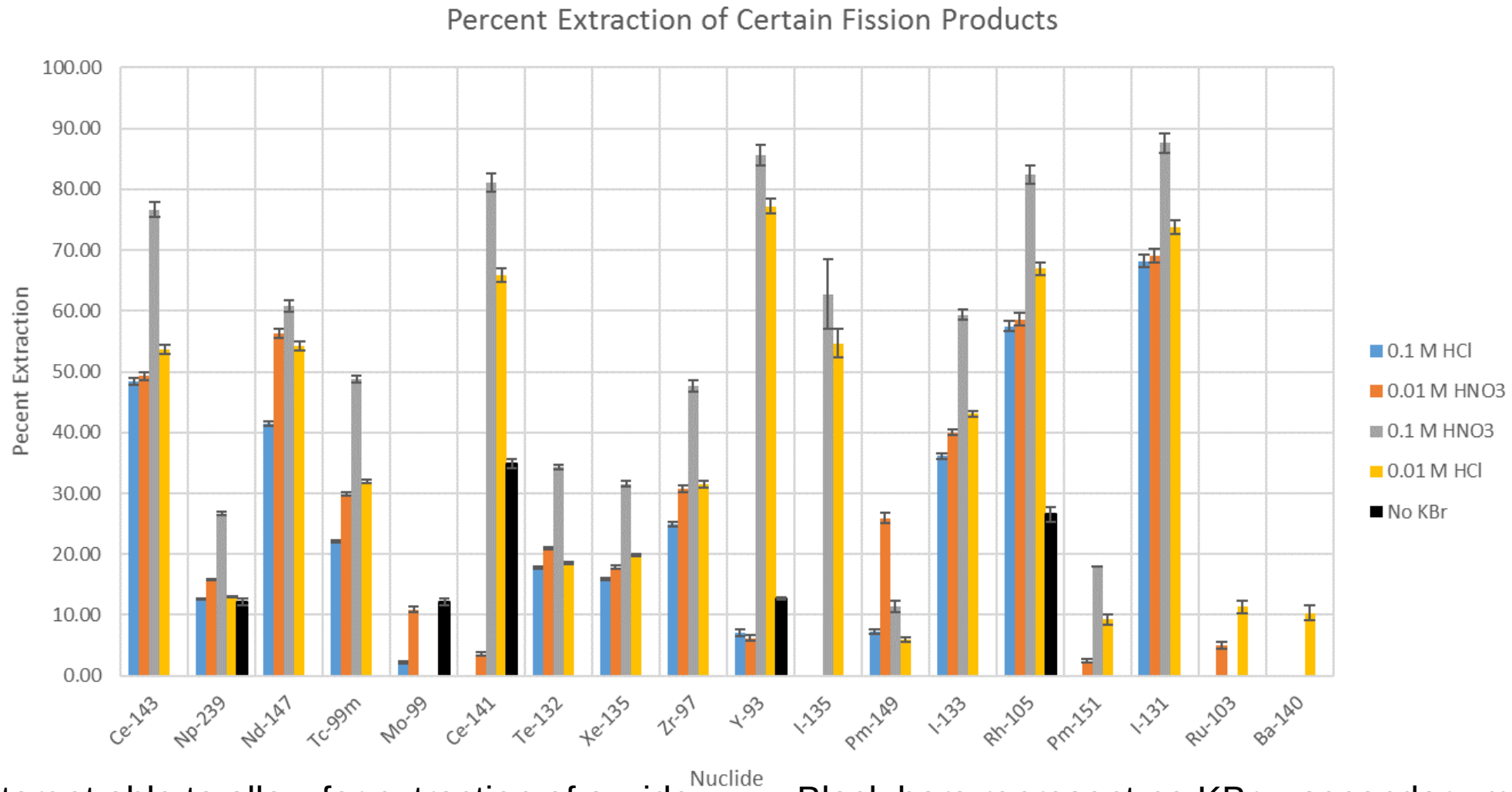
- HPGe and BEGe detectors used in experiments
- Each sample (plus a background) was counted for the same amount of time
- Down-side: only gamma emitting isotopes are identifiable



Results – Flattop Irradiations

- Several irradiations done on multiple samples
- Five UO_2 samples studied
  - Four samples of 3KBr:UO_2
    - Each contacted with a different acid
      - 0.01 M HCl, 0.1 M HCl, 0.01 M HNO_3, or 0.1 M HNO_3
  - One sample with no KBr present
    - How important is secondary matrix?
    - Contacted with 0.01 M HNO_3

Results – Flattop Irradiations



- Each target able to allow for extraction of a wide variety of fission products
- 0.1 M HNO_3 data is artificially high
- Black bars represent no KBr – secondary matrix does have an affect

Issues – Part 1

- KBr is easy to work with and remove with dilute acid, but it is activated in the neutron flux to give ^{82}Br
  - Many gamma energies
  - Short half-life, high activity
  - Could be resolved by using a different secondary matrix
- Targets were irradiated at different times under different conditions
  - Cannot compare activities extracted
  - Must compare percent extraction

Conclusions – Part 1

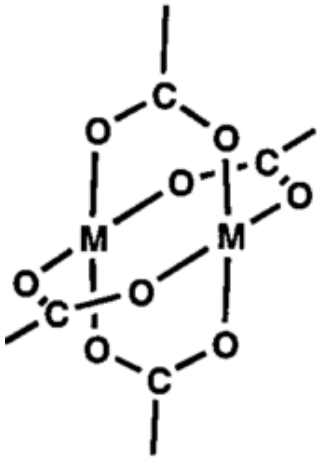
- Proof-of-concept shown
- 0.01 M HNO_3 chosen as extractant for all future experiments
- Secondary matrix does seem to have a positive affect on extraction
- Different secondary matrix could make analysis easier

Nuclear Forensics Part 2

Alternative Target Materials

Background – Metal Organic Frameworks

- MOFs are a porous material where metal centers are linked with organic ligands to form 3D structures



- Most common ligands are dicarboxylic acid based

- Can pores be advantageous for extracting fission products without a secondary matrix?

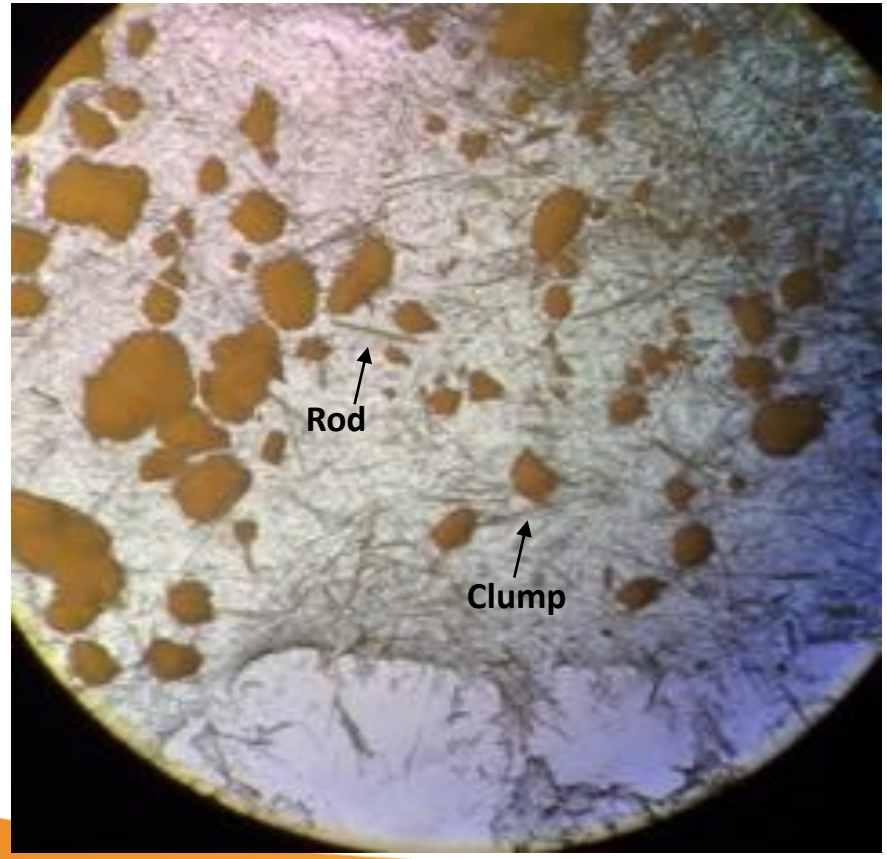
$$UO_2(NO_3)_2 + \text{Ligand} \xrightarrow[H_2O]{150\ ^\circ C} UO_2\text{MOF}$$

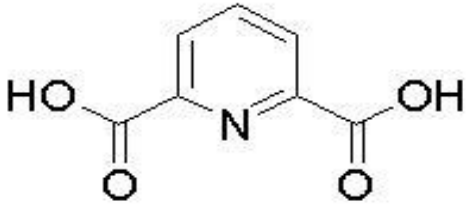
- Four MOFs were studied

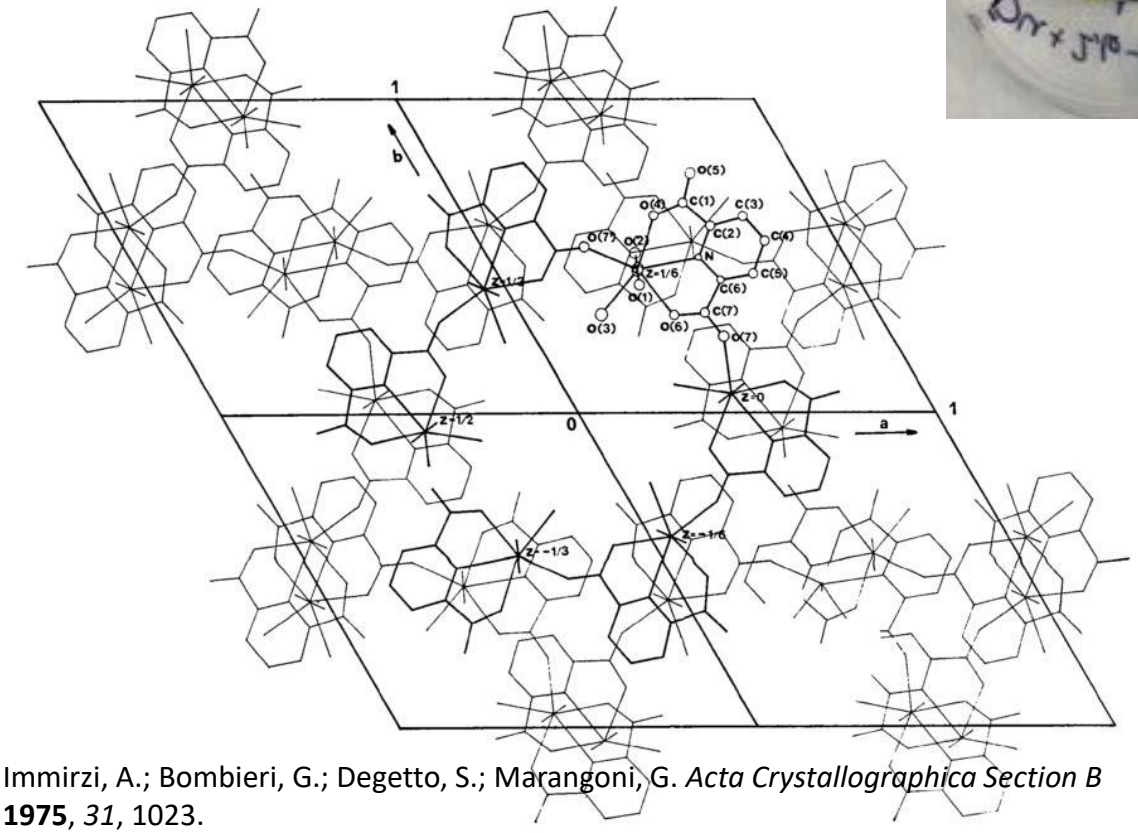
Kim, J.; Chen, B.; Reineke, T. M.; Li, H.; Eddaoudi, M.; Moler, D. B.; O'Keeffe, M.; Yaghi, O. M.
Journal of the American Chemical Society **2001**, *123*, 8239.

Background – UO_2-2,6-pyridinedicarboxylic acid

- UO_2-2,6-pydc

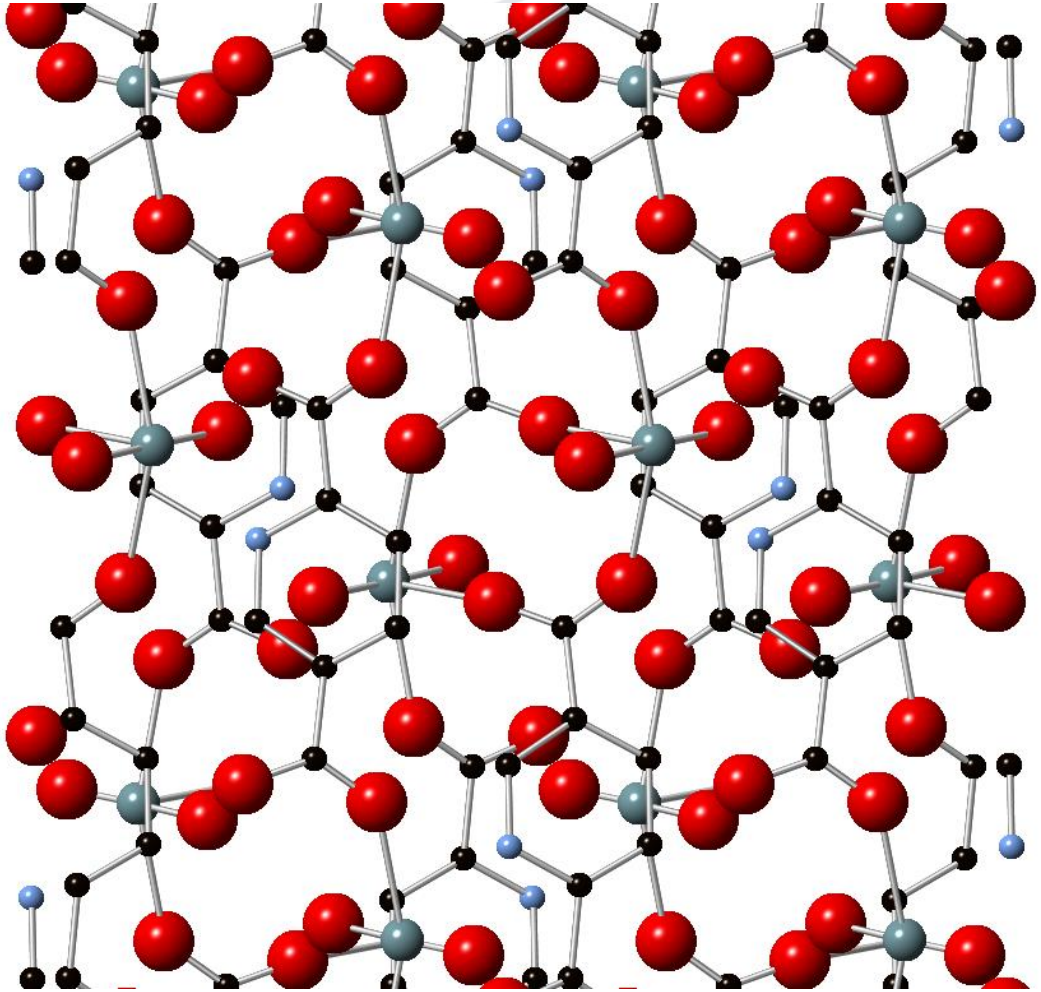


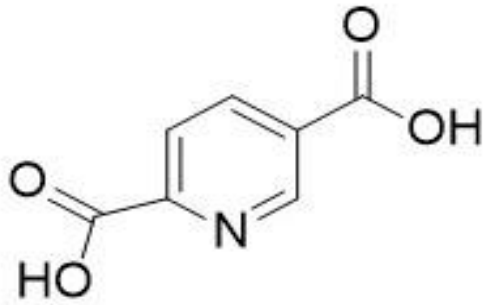


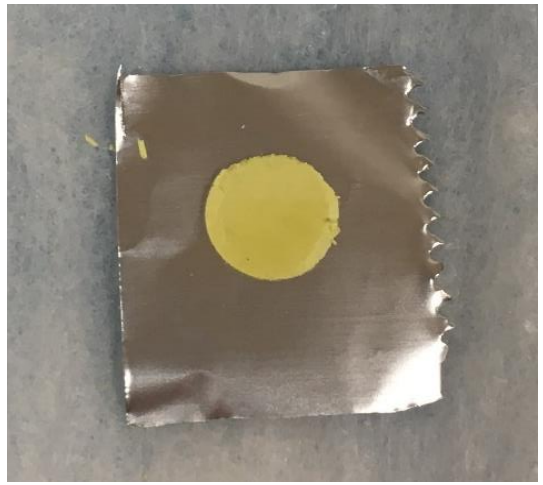


Immirzi, A.; Bombieri, G.; Degetto, S.; Marangoni, G. *Acta Crystallographica Section B* **1975**, *31*, 1023.

Background – UO_2-2,5-pydc



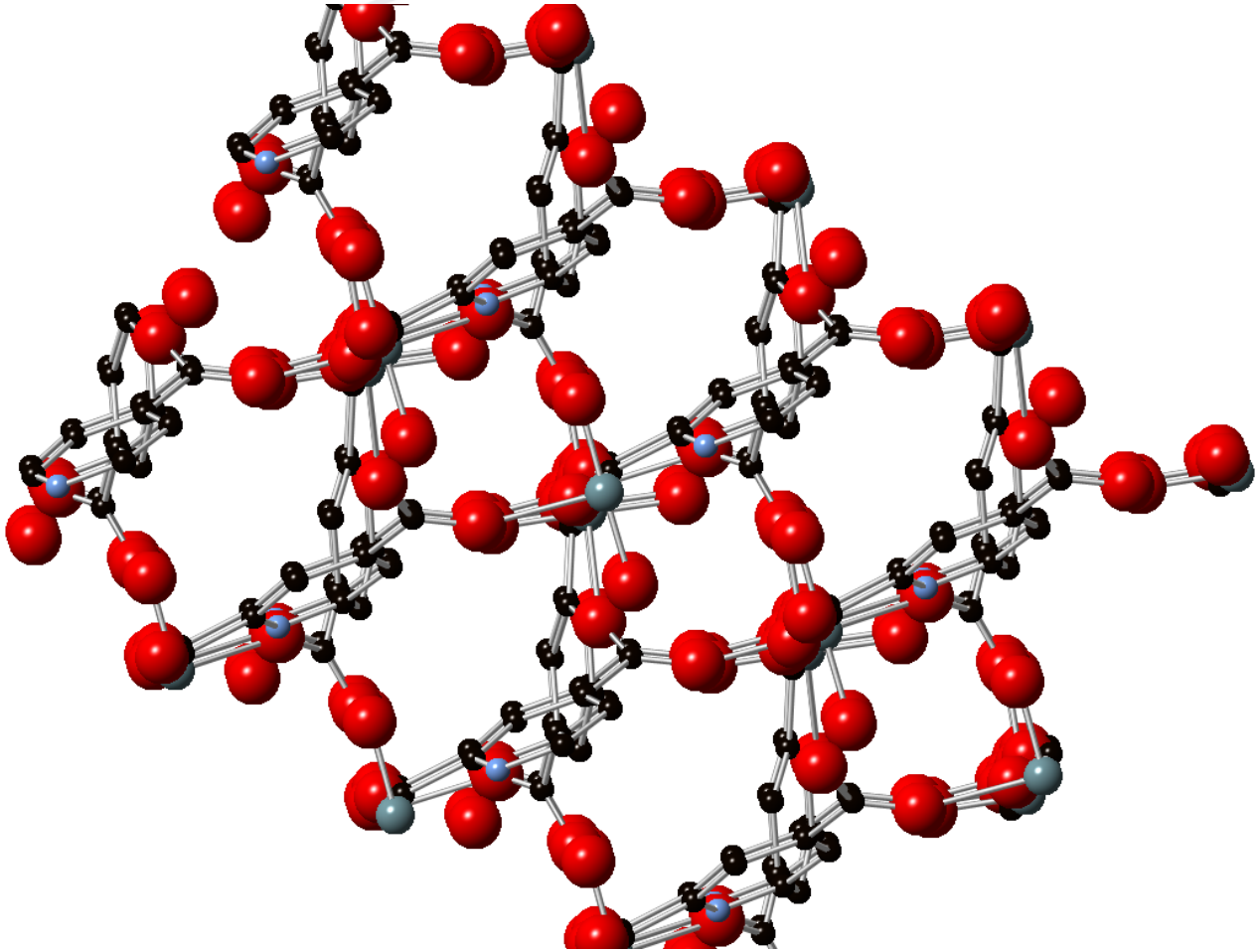


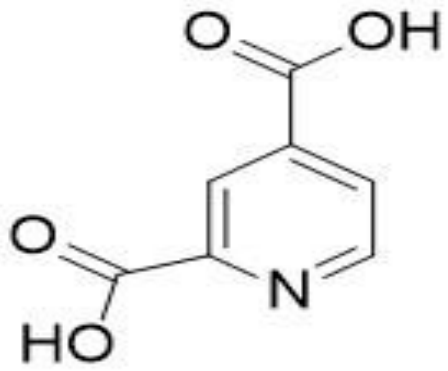


Grey = Uranium
Black = Carbon
Blue = Nitrogen
Red = Oxygen

UNCLASSIFIED

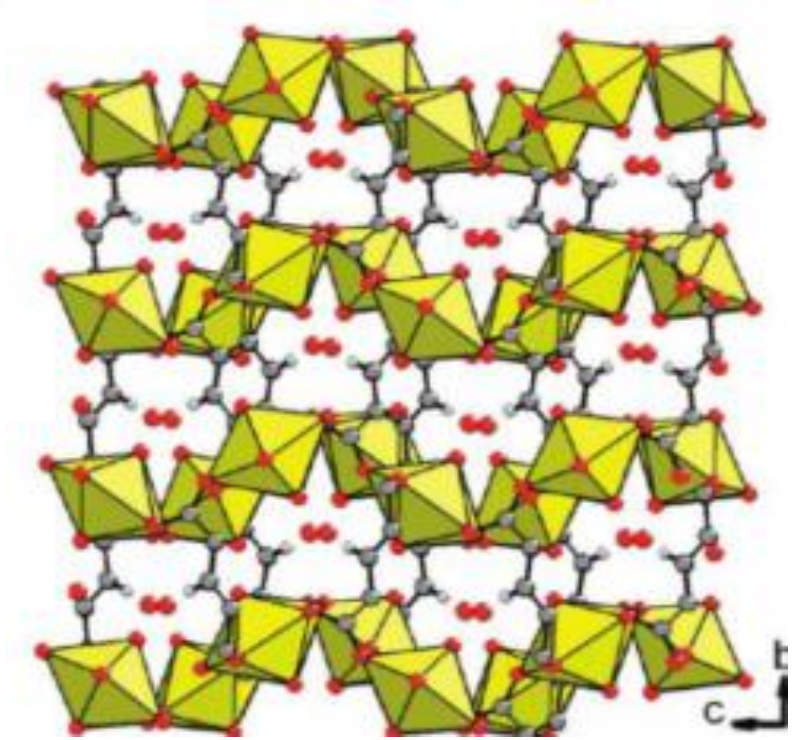
Background – UO_2-2,4-pydc

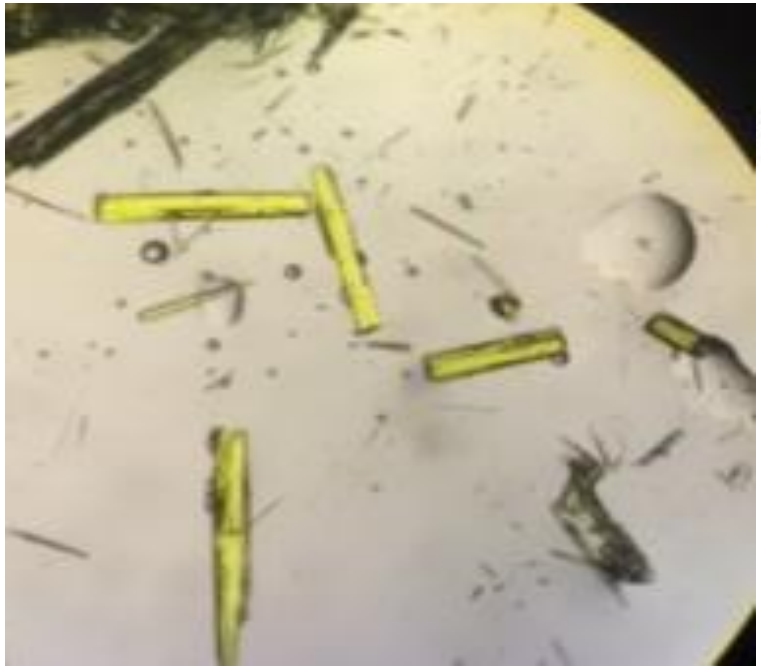


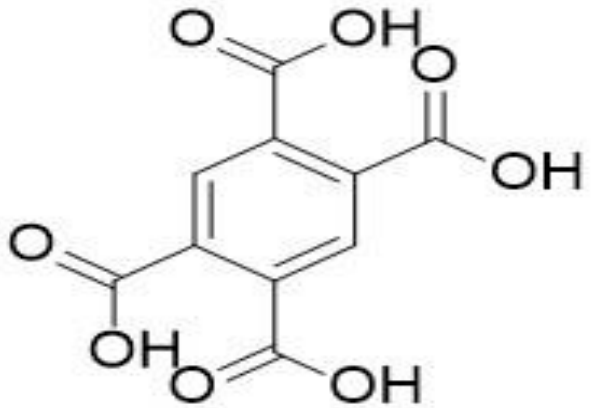


Background – UO_2-pyromellitic acid

- Fourth MOF (UO_2-prma) was a different structure





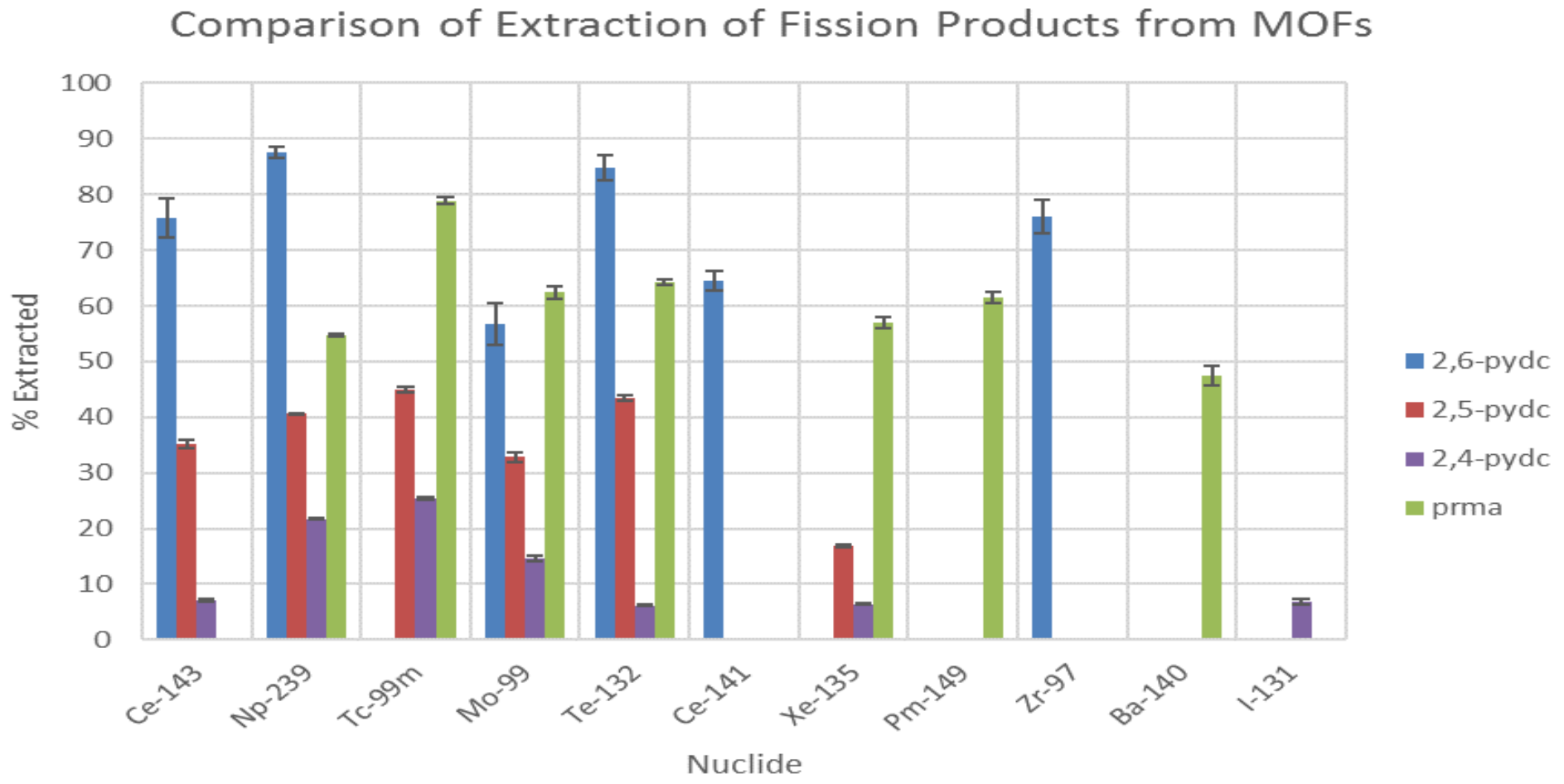


Mihalcea, I.; Henry, N.; Volkringer, C.; Loiseau, T. *Crystal Growth & Design* **2012**, *12*, 526.

Irradiation

- All four MOFs irradiated using Flattop
- Each target was contacted with 0.01 M HNO_3 in the same method as the UO_2 targets
- Prior to irradiation, a sample of each MOF was contacted in acid for 24 hours
  - Any dissolution would be due to irradiation, not material property

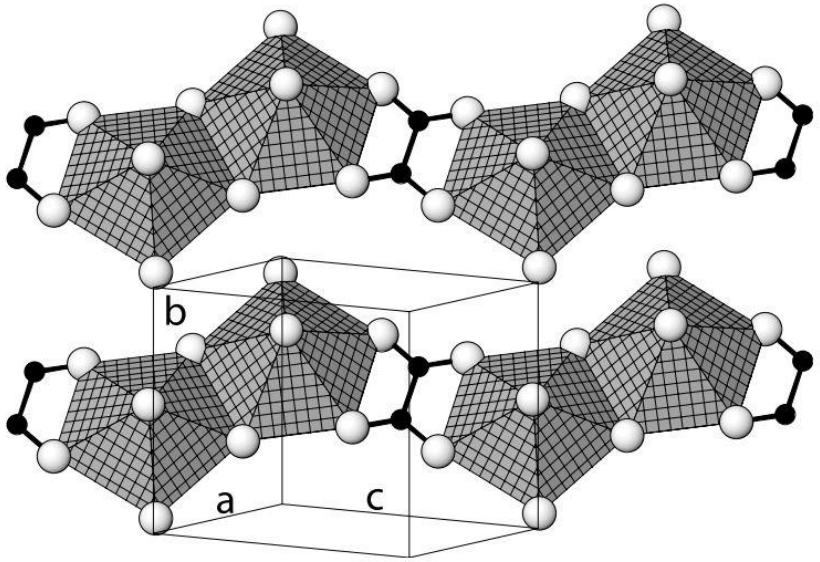
Results - MOFs

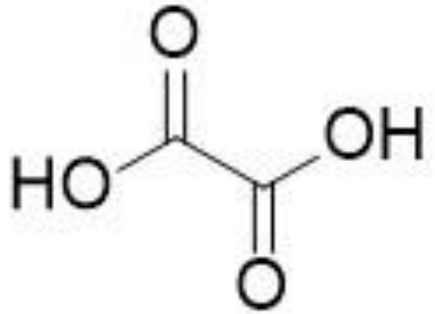


- Smaller pore size leads to less extraction
- UO_2-prma target had different structure and shows best extraction for the most variety of fission products

Background - Oxalate

- UO_2-oxalate is often formed in the processes used to manufacture fuel
- Not technically a MOF, the material is a series of flat polymer sheets linked together with hydrogen bonding



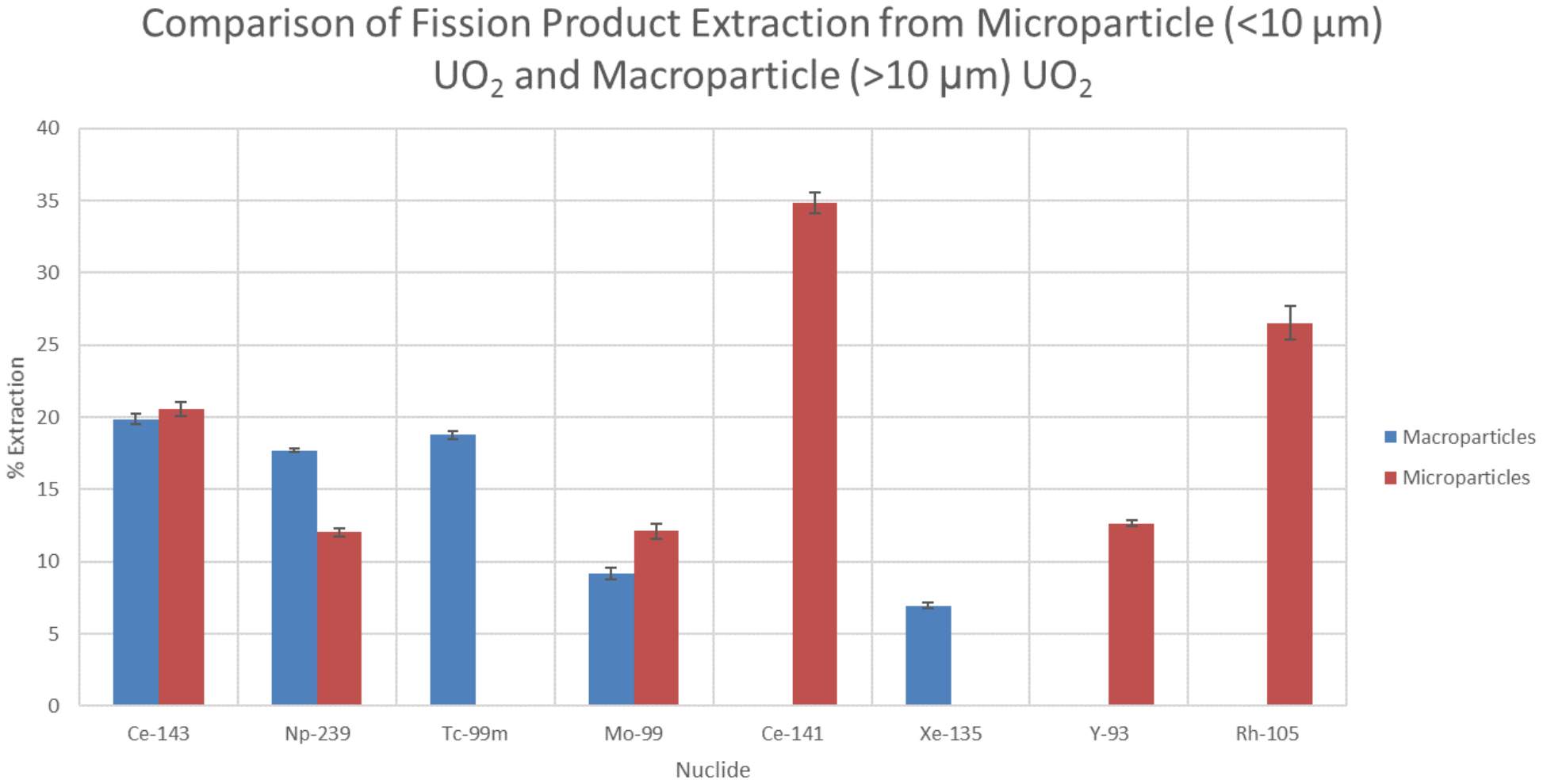


Giesting Paul, A.; Porter Nathan, J.; Burns Peter, C. In *Zeitschrift für Kristallographie - Crystalline Materials* 2006; Vol. 221, p 252.

Results - Oxalate

- Yellow UO_2-oxalate target returned as black UO_2
- No secondary matrix
- Some assumptions:
  - UO_2 is homogenous
  - UO_2 particles are larger than 10 µm

Results - Oxalate



- Compared to microparticle UO_2 target without KBr
- Both contacted with 0.01 M HNO_3
- Microparticles are better for extraction of fission products

Issues – Part 2

- Conditions in Flattop (i.e. temperature) are not ideal for using organic-based materials

- Slight enrichment of materials allows for the use of thermal neutrons (~ 0.025 eV)
  - May negate temperature issues

Conclusions – Part 2

- MOFs can be used for the extraction of fission products, but yield depends on framework type and pore size
- Studying more types of MOFs will give a better correlation
- Some materials are not suited for fast neutron environments and would be better studied in a reactor situation.

Organoactinide Chemistry

Actinide Chalcogenides

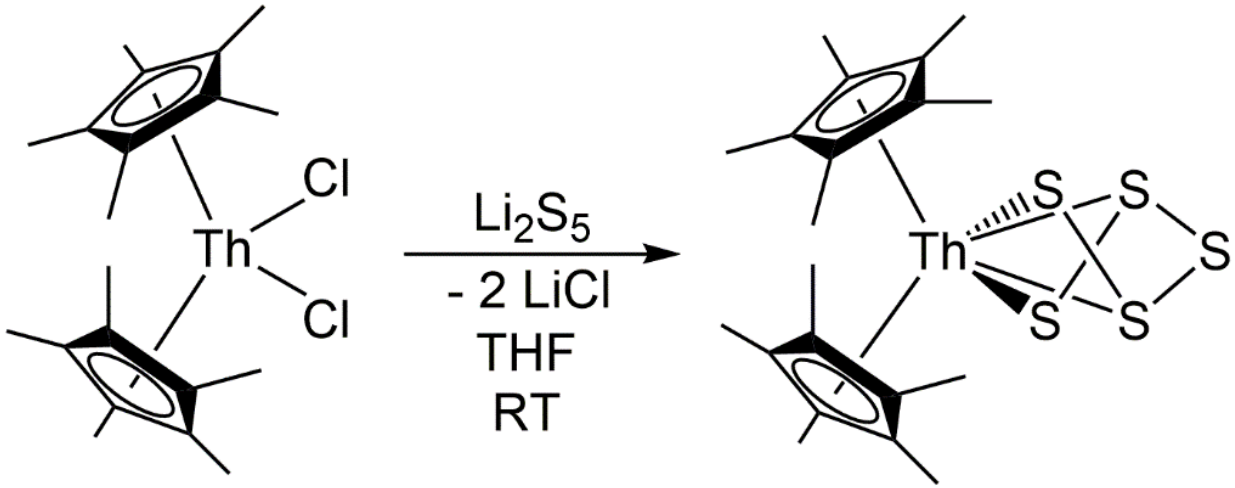
Background

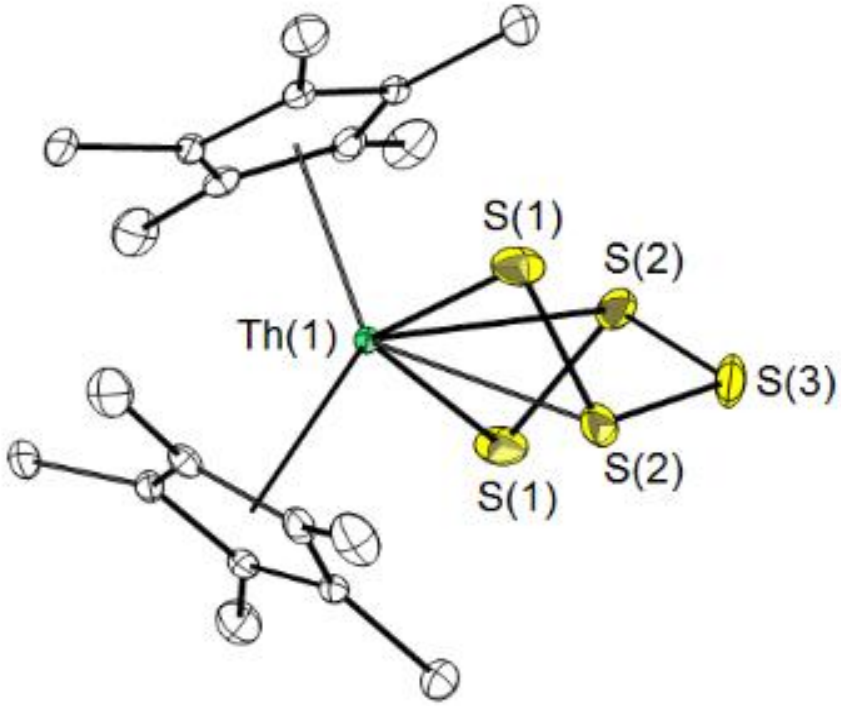
- Chalcogenides (i.e. sulfur, selenium, tellurium) are soft-donor atoms
  - Can be used for separation between lathanides and actinides

- Chemistry of the actinides (hard-donor atoms) with the soft chalcogenides is not well understood but is of interest to both the radiochemical and organoactinide communities.
  - How do 5f-electrons get involved in bonding?
    - Comparisons of thorium (no f-electrons) with uranium can help elucidate

Background

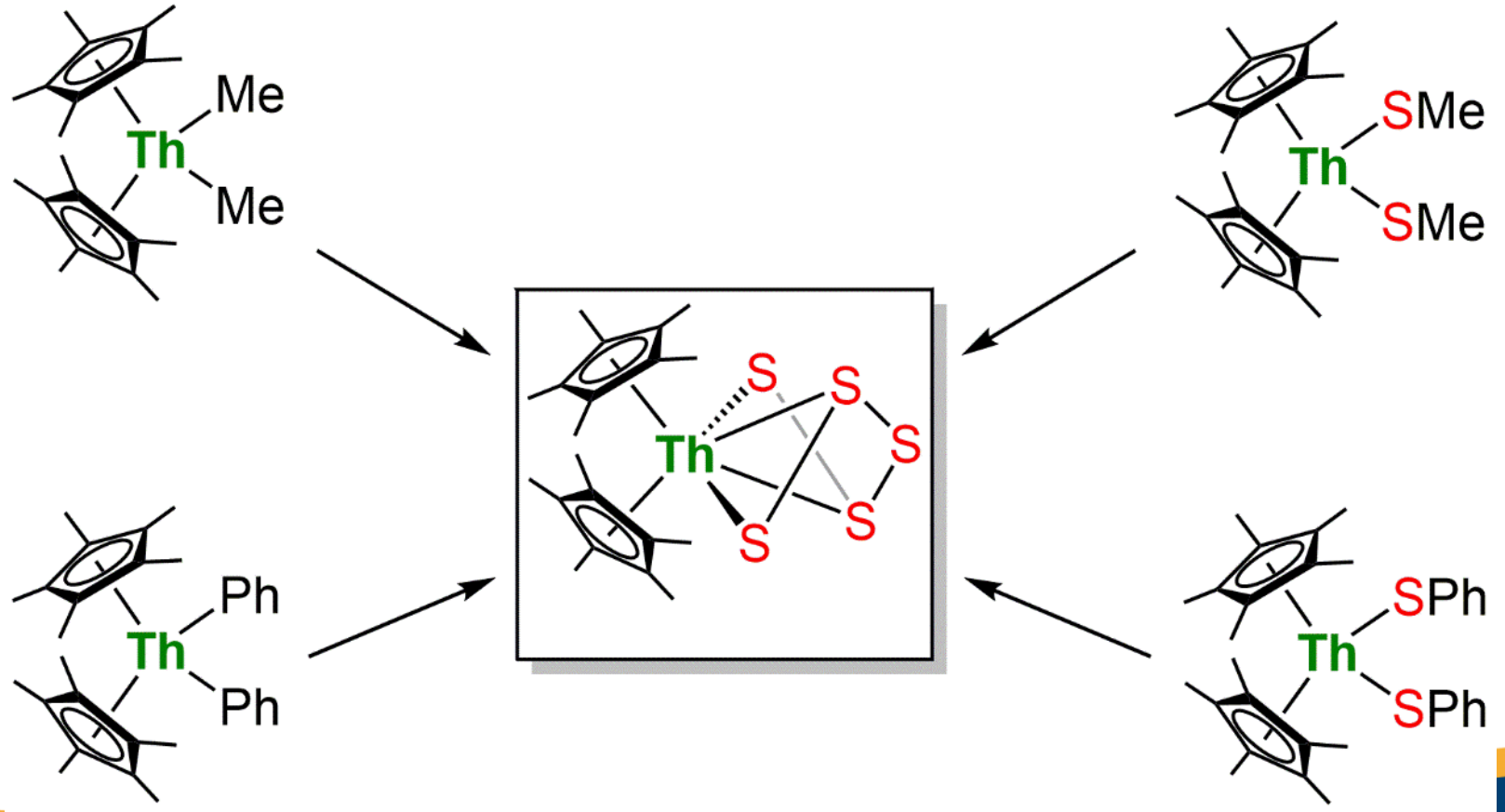
- Sattelberger et.al. published the first organothorium-sulfide in 1986



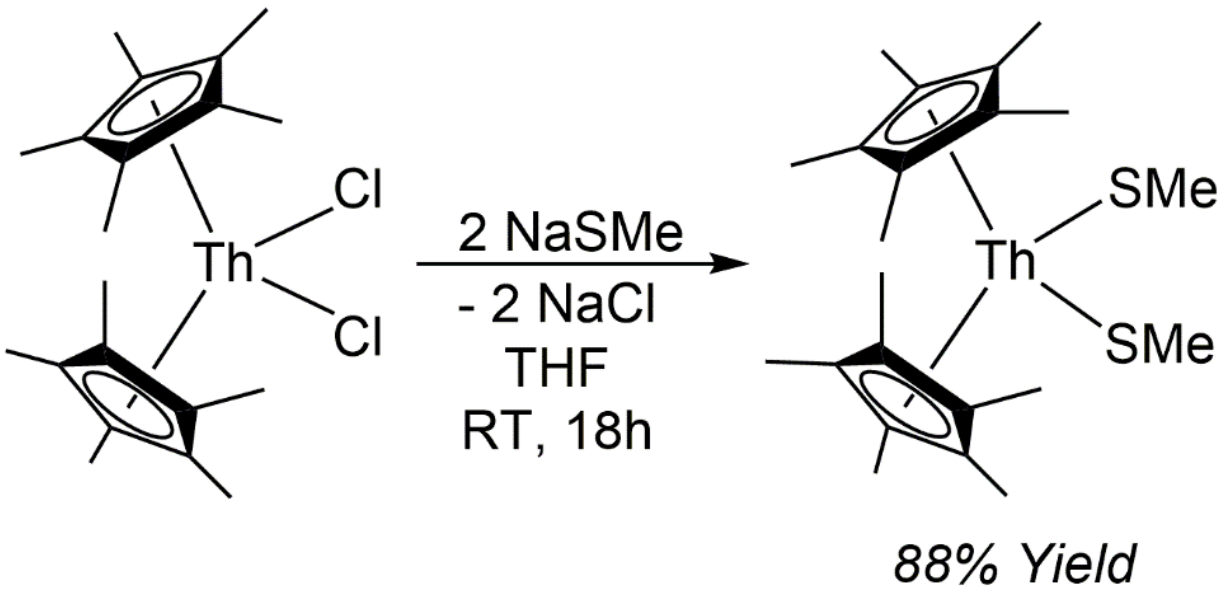


Experimental

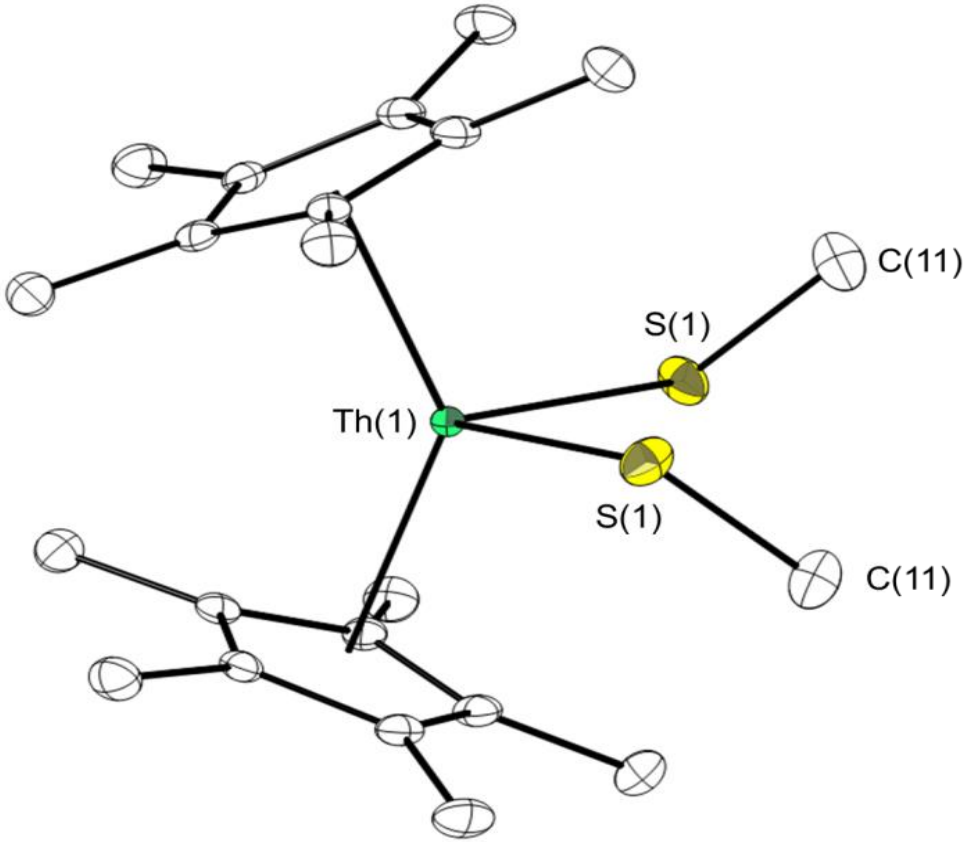
- Kiplinger group was studying insertion of chalcogenides into An-C bonds and found that $(C_5Me_5)_2ThS_5$ is a thermodynamic sink



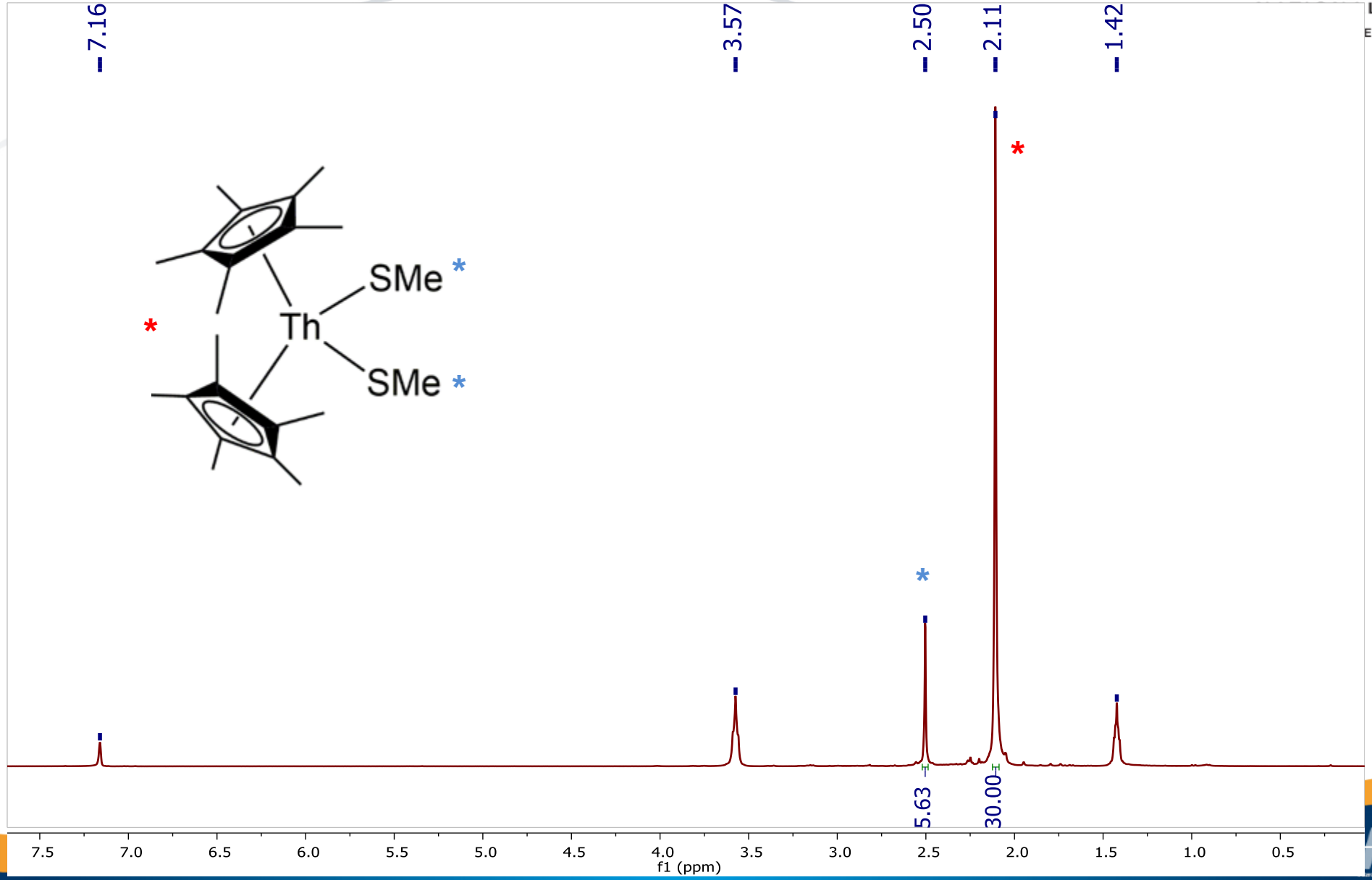
Experimental



88% Yield

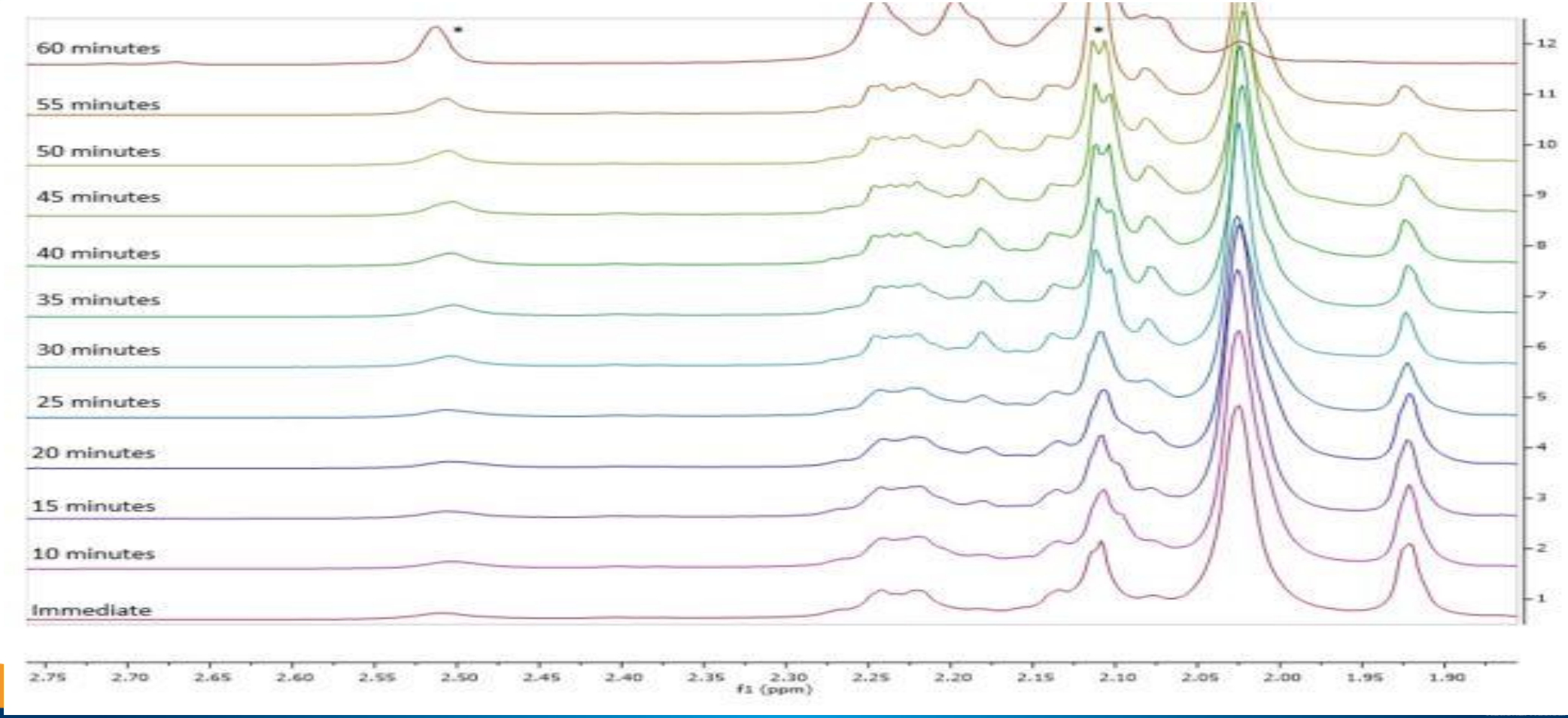


Experimental



Results

- Monitoring the reaction of $(C_5Me_5)_2ThMe_2 + S_8$ by NMR showed intermediate formation of $(C_5Me_5)_2Th(SMe)_2$

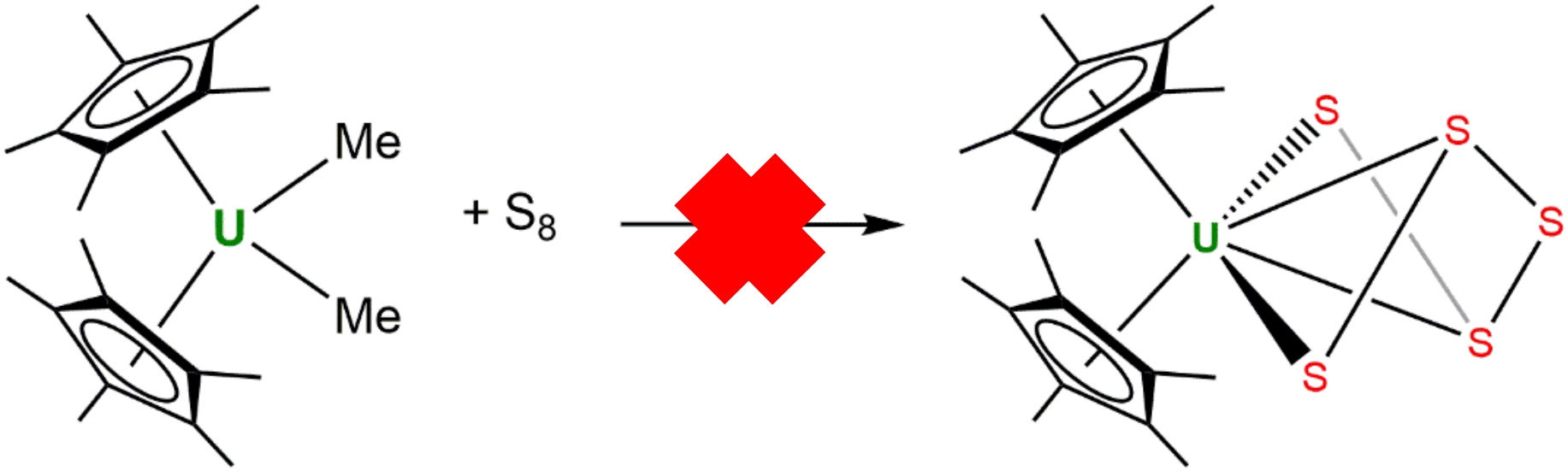


Results

- Formation of MeSSMe, MeSMe, and MeSSSMe is also seen by NMR

- $(C_5Me_5)_2Th(SMe)_2$ appears to undergo side reactions with these byproducts, but final product is always $(C_5Me_5)_2ThS_5$

Results



Conclusions

- There is sulfur insertion between thorium and carbon of methyl group
- Novel complex $(C_5Me_5)_2Th(SMe)_2$ reported and characterized
- Uranium chemistry doesn't behave analogously

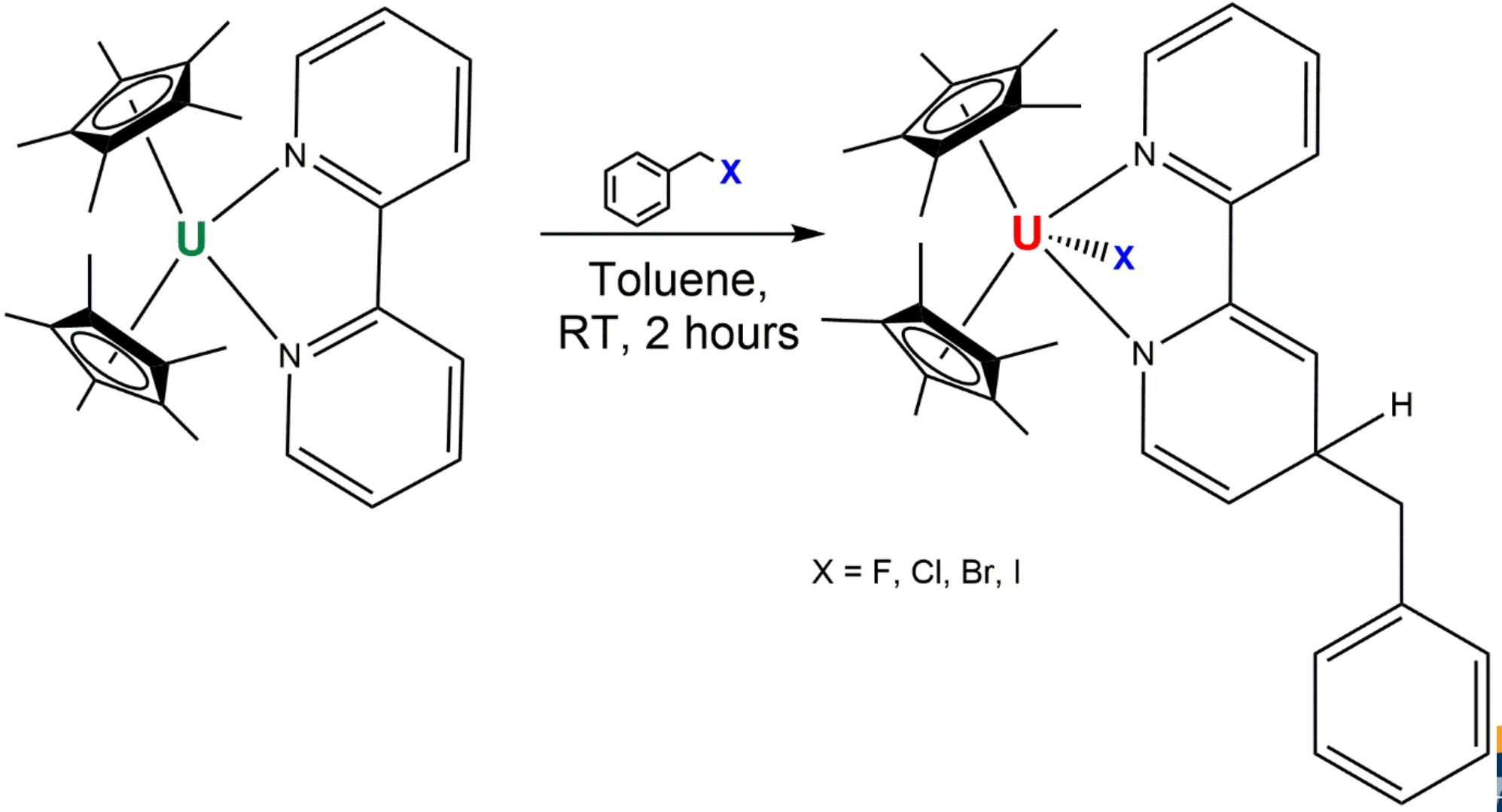
Organoactinide Chemistry

C – X Activation

Background

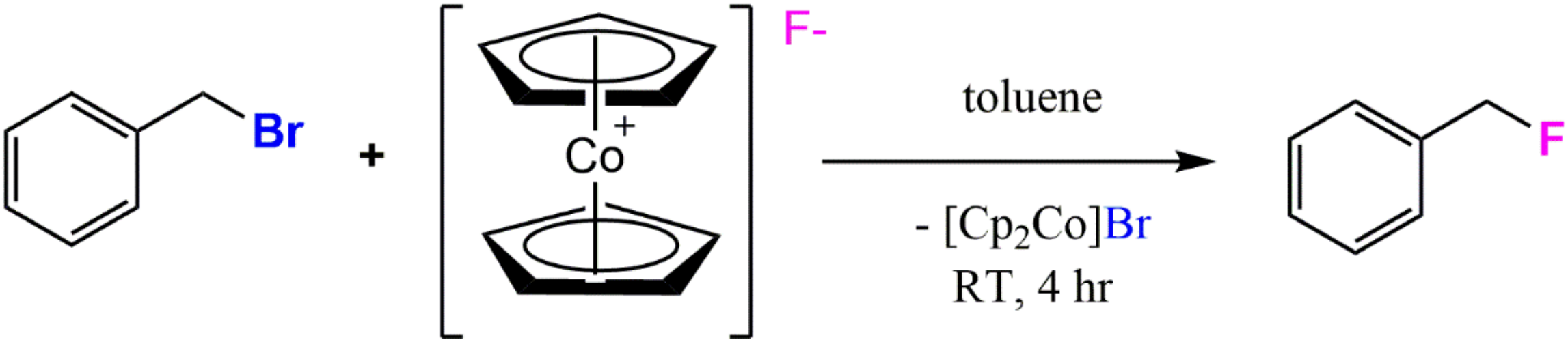
- Transition metal mediated C–X activation (X = H, F, Cl, Br, I) has been studied as a route to novel organometallic compounds
- Actinide studies are lacking in the literature
  - There are examples of C–H activation with uranium
  - C–N bond activation with thorium-bipyridine complexes
- Important to understand how actinides can interact with halide environments

Experimental

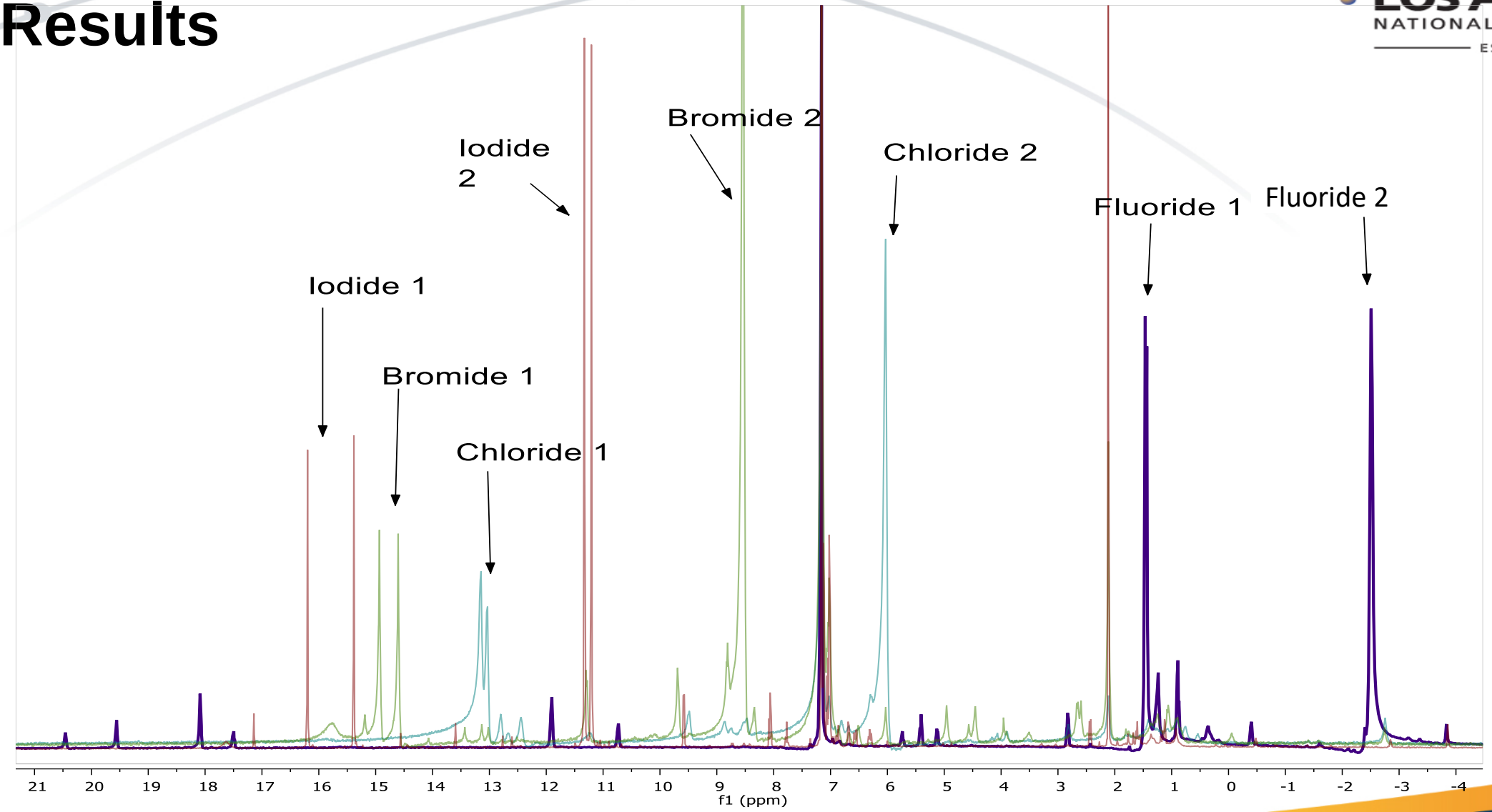


X = F, Cl, Br, I

Experimental

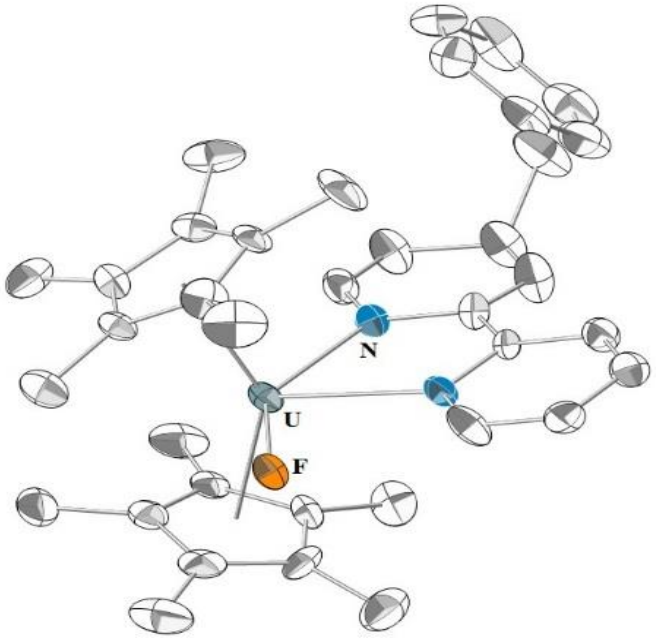


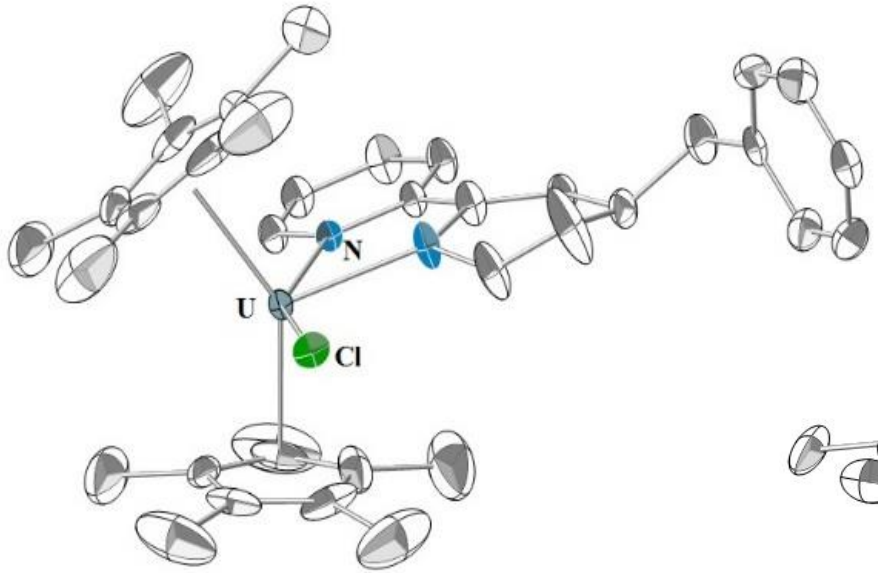
Results

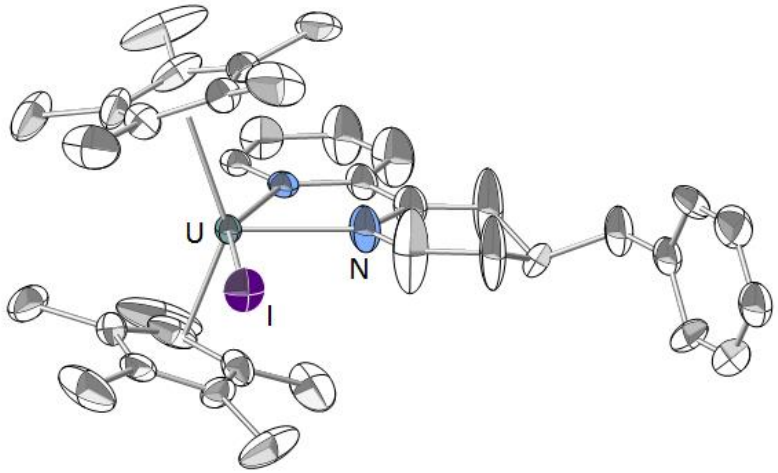


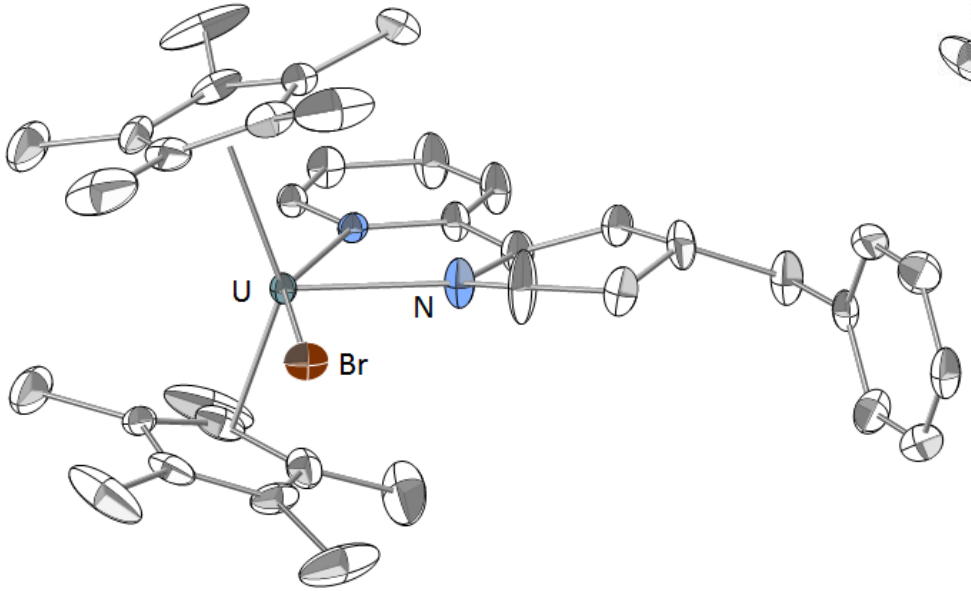
UNCLASSIFIED

Results

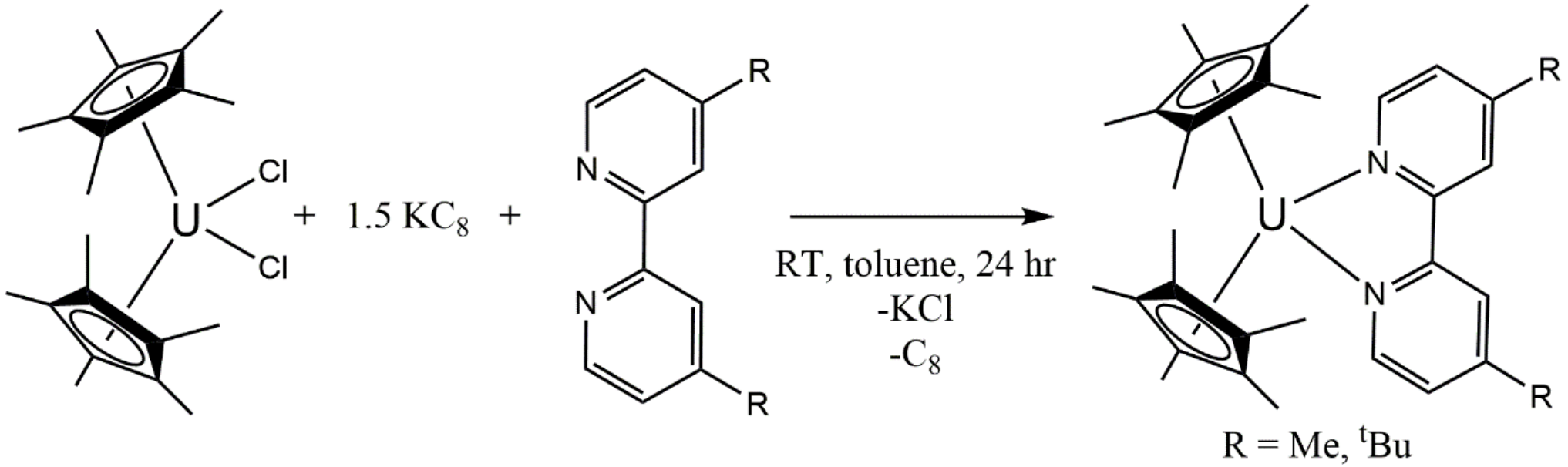




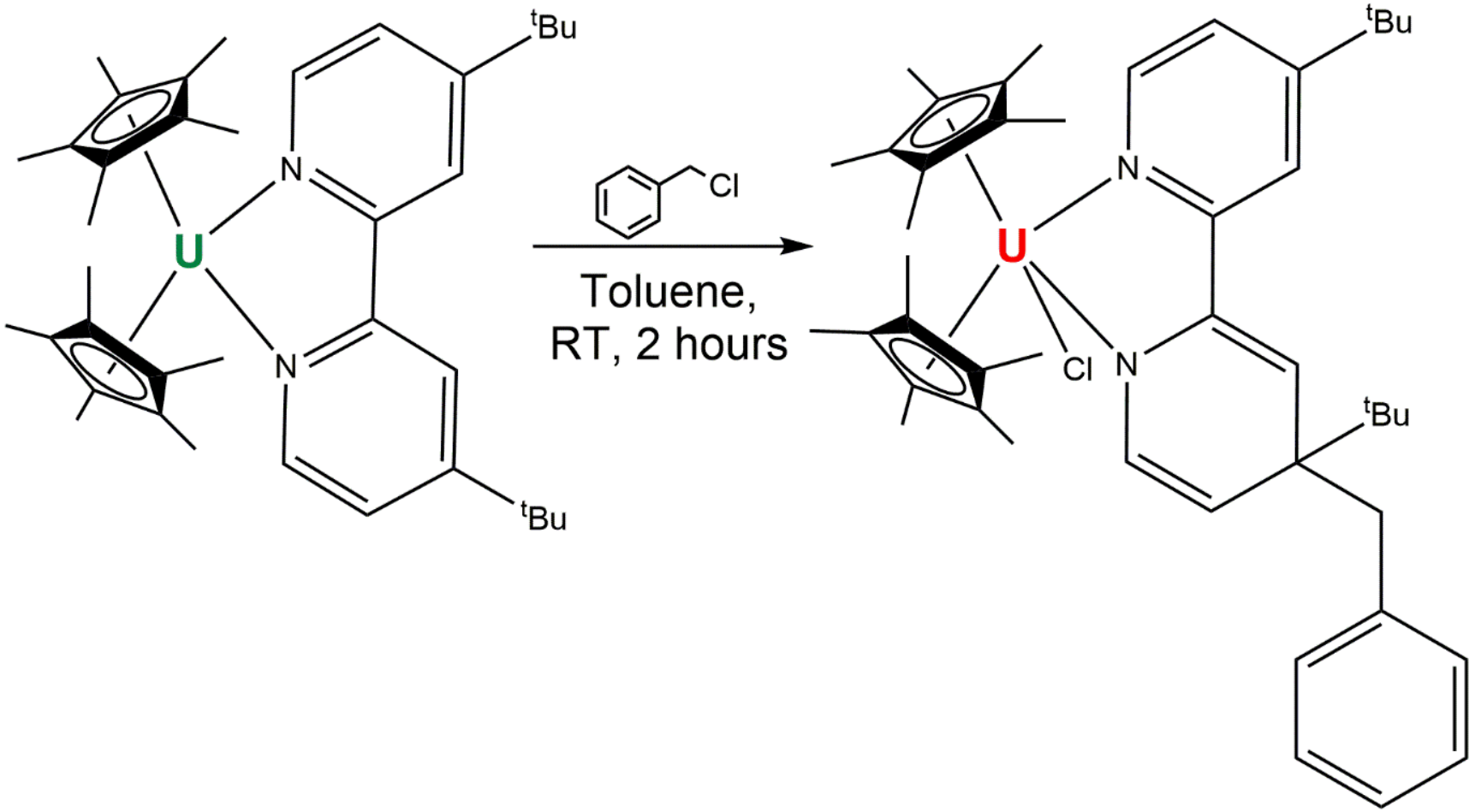


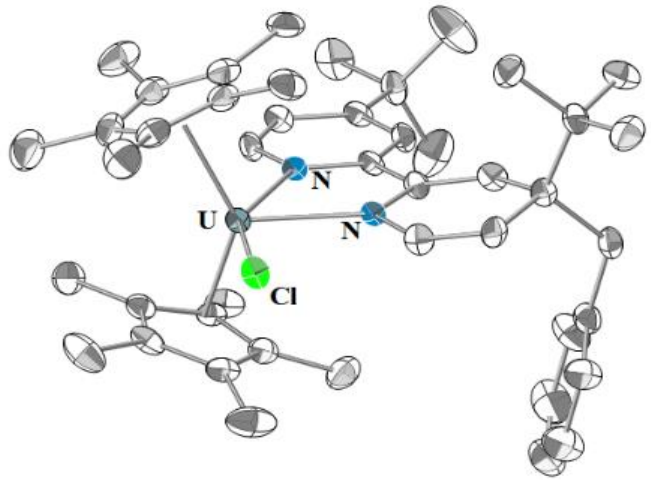


Experimental

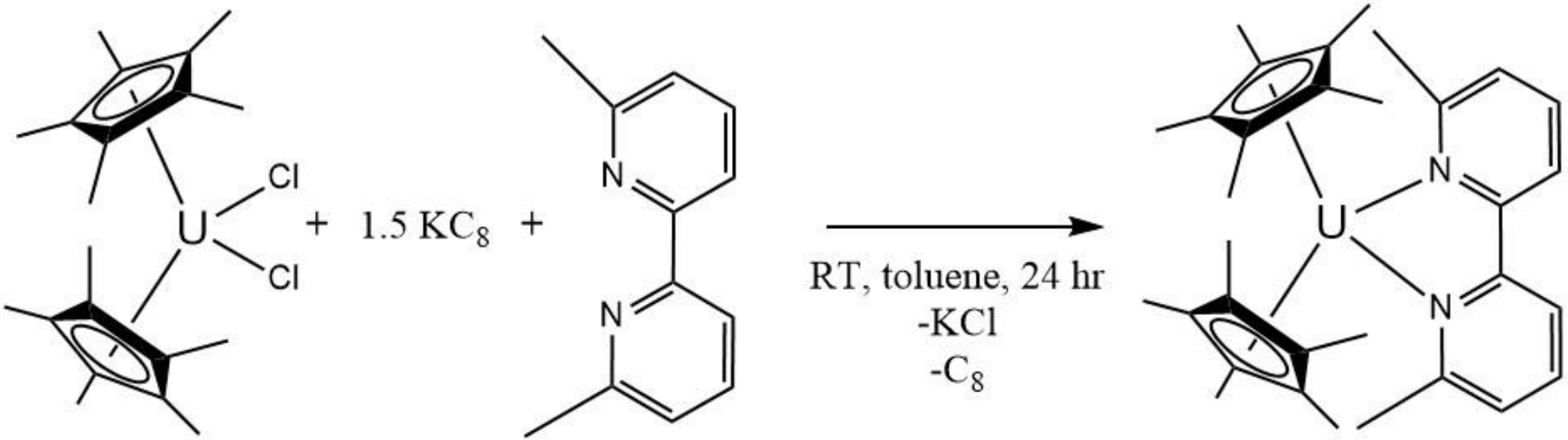


Results

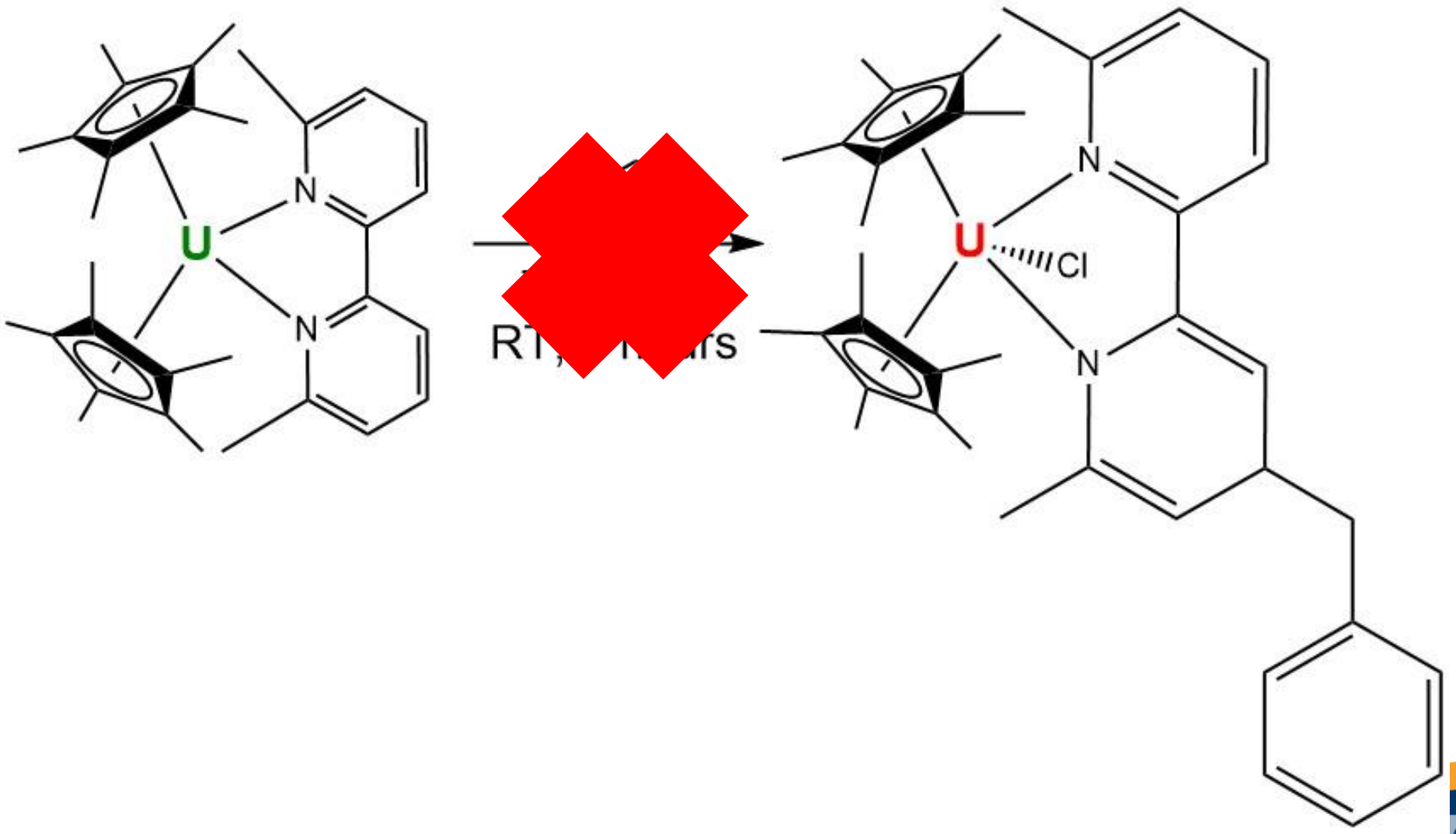




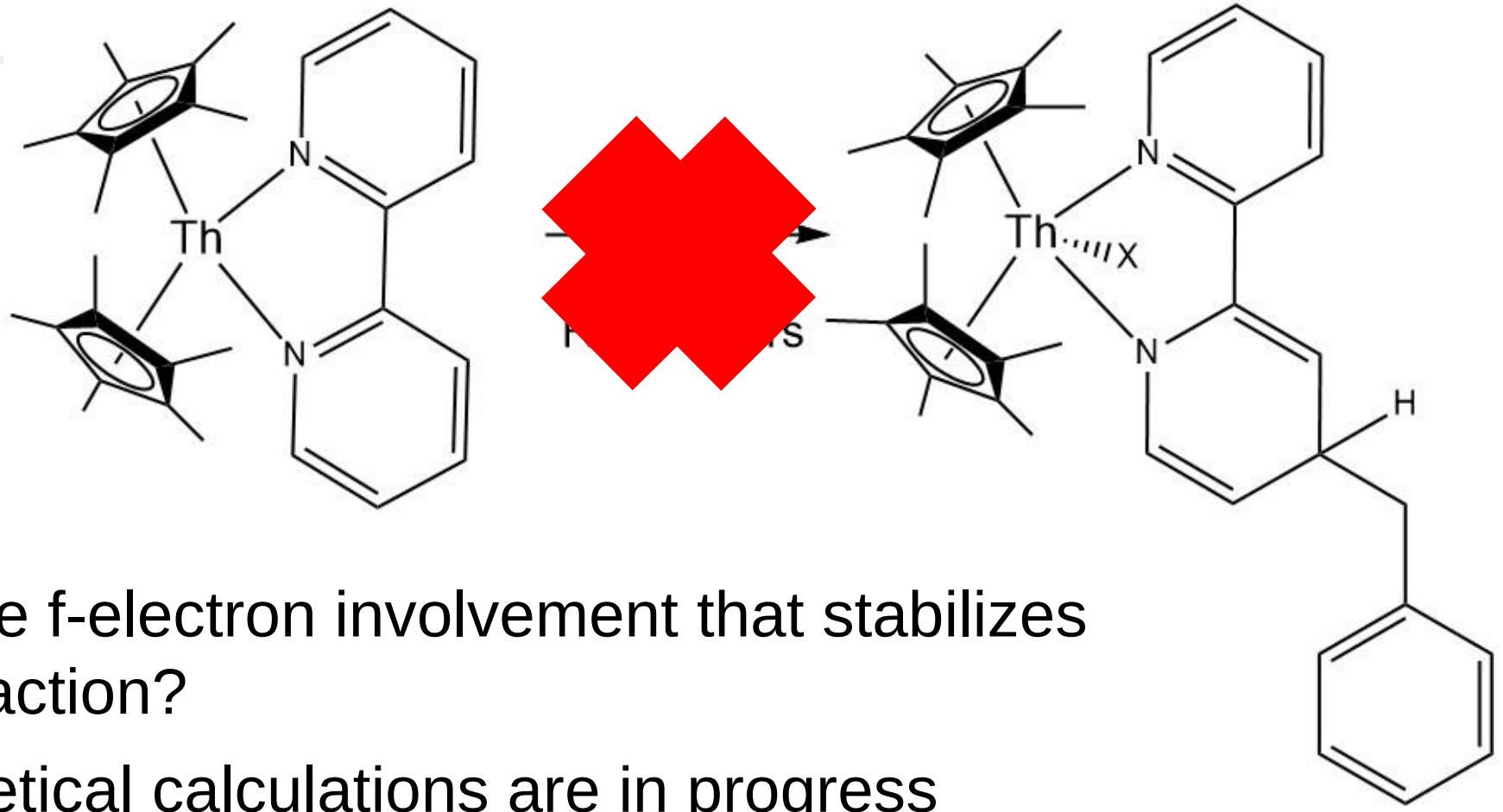
Experimental



Results



Experimental - Thorium



- Is there f-electron involvement that stabilizes the reaction?
- Theoretical calculations are in progress

Conclusions

- Series of U-X (X = F, Cl, Br, I) complexes were formed using actinide mediated C–X activation
  - The benzyl group adds across the bipyridine rings

- Preliminary exploration into the mechanism seems to show that it is a migration rather than addition of the benzyl

- Chemistry does not work for thorium analog

Summary and Future Work

Summary – Part 1

- Proof-of-concept that an actinide target can be used to rapidly separate fission products without dissolving the target
  - Use of a secondary matrix (i.e. KBr) increases the yield

Future Work – Part 1

- Use a secondary matrix that is not activated
- Use a different isotope, or combinations of isotopes
- Use of $^{237}NpO_2$ to form ^{238}Pu

Summary – Part 2

- MOFs can also be a useful target, depending on pore size and framework structure
- Use of smaller particles of UO_2 increases yield

Future Work – Part 2

- Study a variety of other MOFs
- Change the metal
- Enrich sample and use thermal neutrons

Summary – Organoactinide Story

- Novel thorium sulfide
- Mechanism to understand $(C_5Me_5)_2ThS_5$

- C–X activation using uranium to give a suite of novel uranium-halide compounds
- Rare example of a U–F bond
- Rare example of activation and addition across a bipyridine ligand

Future Work – Organoactinide Story

- Synthesis of $(C_5Me_5)_2US_5$ for comparison to thorium

- Theoretical explorations into C–X activation mechanism

Acknowledgements

- Thesis Committee
  - Dr. Ken Czerwinski
  - Dr. Ralf Sudowe
  - Dr. Paul Forster
  - Dr. Jaqueline Kiplinger
  - Dr. Alex Barzilov
- UNLV
  - Dr. Thomas Hartmann
  - Dr. Dan Koury
  - Julie Bertoia
  - Trevor Low
  - Daniel Mast
  - Dr. Daniel Lowe, Dr. Bill Kerlin, Rebecca Springs, Lucas Boron-Brenner
  - Radiation Safety Staff
  - Radiochemistry group
- LANL
  - Drs. Karla Erickson, Justin Pagano, Stephen Cope, Ross Beattie, Marisa Monreal, David Morris, Jacqueline Veauthier, George Stanley
  - Drs. Nick Travia, Kevin Browne, Alex Lichtscheidl
- DAF
  - Dr. Todd Bredeweg
  - Dr. Donnette Lewis
  - Radiation and Safety Staff
- Family and friends
- Funding
  - NTNFC fellowship
  - Glenn T. Seaborg Institute for Transactinium Science GRA Fellowship
  - DOE Office of Basic Science

This material is based upon work supported by the U.S. Department of Homeland Security under Grant Award Number, 2012-DN-130-NF0001-02.

The views and conclusions contained in this document are those of the authors and should not be interpreted as necessarily representing the official policies, either expressed or implied, of the U.S. Department of Homeland Security.

References

- Prelas, M. A.; Weaver, C. L.; Watermann, M. L.; Lukosi, E. D.; Schott, R. J.; Wisniewski, D. A. *Progress in Nuclear Energy* **2014**, *75*, 117
- Blakemore, P.; Oregon State University: Corvallis, Oregon, 2017; Vol. 2017, p image of parr bomb.
- Krishnan, M. *IEEE Transactions on Plasma Science* **2012**, *40*, 3189
- Brewer, R. W.; McLaughlin, T. P.; Dean, V. *Uranium-235 Sphere Reflected by Normal Uranium Using Flattop*, Nuclear Energy Agency, 1999.
- Kim, J.; Chen, B.; Reineke, T. M.; Li, H.; Eddaoudi, M.; Moler, D. B.; O'Keeffe, M.; Yaghi, O. M. *Journal of the American Chemical Society* **2001**, *123*, 8239.
- Immirzi, A.; Bombieri, G.; Degetto, S.; Marangoni, G. *Acta Crystallographica Section B* **1975**, *31*, 1023.
- Mihalcea, I.; Henry, N.; Volkringer, C.; Loiseau, T. *Crystal Growth & Design* **2012**, *12*, 526.
- Giesting Paul, A.; Porter Nathan, J.; Burns Peter, C. In *Zeitschrift für Kristallographie - Crystalline Materials* 2006; Vol. 221, p 252.
- Bennett Brian, K.; Harrison, R. G.; Richmond, T. G. *Journal of the American Chemical Society* **1994**, *116*, 11165.
- Browne, K. P.; Maerzke, K. A.; Travia, N. E.; Morris, D. E.; Scott, B. L.; Henson, N. J.; Yang, P.; Kiplinger, J. L.; Veauthier, J. M. *Inorganic Chemistry* **2016**, *55*, 4941.